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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

CL

SEPTEMBER, 1908

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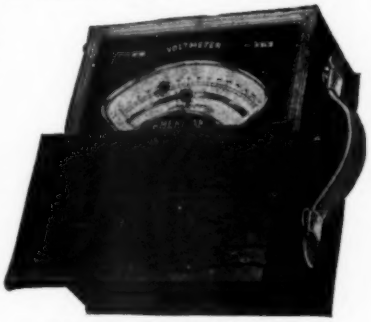

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THE

PHYSICAL REVIEW.

THE EFFECT OF CONCENTRATION AND IONIZATION ON THE RATES OF DIFFUSION OF SALTS IN AQUEOUS SOLUTION.[1]

By Raymond Haskell.

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1. Introduction.

According to the modern theory of solutions the osmotic pressure in a solution is proportional to the concentration of the solute. If now there is a difference of osmotic pressure between two points, there is a tendency for the solute to move from the region of higher to that of lower pressure, and the rate of this movement is proportional directly to the difference in pressure or concentration and inversely to the resistance of the medium. If the amount of the solvent is large in comparison with that of the solute this resistance is independent of the concentration of the substance. In the case where an ordinary inorganic salt is the solute the simplicity of this relation may be influenced by the change

[1] Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 26.

taking place with change of concentration in the character of the solute due to ionization. The ions in a solution act osmotically in a manner similar to the undissociated molecules, exerting a pressure proportional to their concentration ; but the frictional resistance which they encounter is different from that of the undissociated substance. Although any difference in the resistance to the motion of the separate ions would tend to cause the faster one to diffuse more rapidly and thus separate it from the others, yet it is held back by the great electrostatic charge which would thus be generated, so that a positive and negative ion of the substance must move together ; but the resultant effect will in general be to produce a rate of diffusion different from that of the undissociated part.

Assuming that the salt was totally ionized Nernst in 1888[1] derived an expression for the rate of diffusion based upon values of the equivalent conductance of the ions as determined by transference and conductivity measurements at great dilution. These calculated values checked very well with experimentally found ones when the experiments were carried on at great dilutions but deviated more and more as the concentration increased. This variation is probably due to the increasing part taken in the diffusion by the undissociated substance as the concentration increases ; and it is the purpose of this investigation to determine the difference in mobility existing between the dissociated and undissociated portions of the solute.

In order to simplify the calculations, the work was restricted to the case of diffusion in one direction only. This was accomplished by using a cylindrical tube filled with pure water at the start, but having a saturated solution at the bottom, thus allowing the diffusion to take place against gravity. The concentration changes were determined by measurement of the electrical conductivity at different points along the tube after various intervals of time. These values substituted in the proper formula allowed the separate diffusion constants of the ions and of the undissociated substance to be calculated. The salts thallium sulphate and barium nitrate were selected as they are to a large extent undissociated in 0.100 normal solutions.

[1] Z. Phys. Chem., *2*, 613, 1888.

2. Theoretical Principles Relating to Diffusion.

General Law of Diffusion.—Although osmotic phenomena as such were not recognized until a later date, its principles were first applied to diffusion by Fick, who in 1854,[1] expressed the law that the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near to each other. That is, if we take two points in a solution at an infinitesimal distance apart dx, the difference in concentration at these two points will be dc and hence the concentration gradient in the direction x will be $\partial c/\partial x$. Fick's law states that, for the case when the diffusion is in one direction only, as occurs when it is allowed to take place in a cylinder, the amount of solute dS which will cross a given cross-section a in a time dt is expressed by

$$dS = -Da\frac{\partial c}{\partial x}dt \qquad (1)$$

or the rate of change by

$$\frac{dS}{dt} = -Da\frac{\partial c}{\partial x}. \qquad (2)$$

The minus sign here denotes that the solute diffuses in the direction of decreasing concentration. D is the so-called diffusion-constant or specific diffusion-rate; it is equal to the amount of solute which would diffuse across unit area under a concentration gradient of unity in unit time if the rate were constant during that time. In this work the time is expressed in days, the concentration in equivalents per liter, and the distance in centimeters.

In the above equation we have two independent variables x and t, and two dependent ones S and c. By the following considerations we can reduce the dependent variables to one. Consider an infinitesimal volume in a cylinder bounded by planes at the distance x and $x+dx$. The amount of solute which will accumulate in this volume in time dt will be the difference in the amount which will cross the planes at x and at $x+dx$. This may be written $-\partial(dS)/\partial x \cdot dx$ since the amount which will cross at $(x+dx)$ equals

$$\left(dS + \frac{\partial(dS)}{\partial x}dx\right).$$

[1] Pogg. Ann., *94*, 59, 1855.

The increase in concentration of the solute in time dt in this volume then is the total accumulation divided by the volume or

$$\frac{-\frac{\partial(dS)}{\partial x}dx}{adx}.$$

As this may also be expressed by the quantity $\partial c/\partial t \cdot dt$ we get

$$\frac{\partial c}{\partial t}dt = -\frac{1}{a}\frac{\partial(dS)}{\partial x}.$$

Substituting for dS its value $-Da \cdot \partial c/\partial x \cdot dt$ given by Fick's law, carrying out the differentiation, and eliminating dt we get as our reduced equation for the case the cross-section is uniform

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{3}$$

This equation is analogous to that of Fourier for the flow of heat, and has different solutions according to the conditions imposed by the methods of carrying out the diffusion. If in a tube so long as to be practically infinite, so far as the time of an ordinary experiment is concerned, the concentration is held constant at one end and is zero at the other, and if at the start the concentration is zero throughout the tube, we may obtain by solving the differential equation under the assumption that D is constant the following expression for the concentration c at any point x after any time t.

$$c = c_0\left(1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}\right) \tag{4}$$

where c_0 is the constant concentration at the lower end, and

$$u = \frac{x}{2\sqrt{Dt}}.$$

Knowing the value c for any point we can inversely calculate D the diffusion constant. If D is not constant for all values of c, as is the case if the assumption of the different rates of diffusion of the dissociated and undissociated substances is true, another formula must be developed which will take this fact into consideration.

Diffusion of Completely Ionized Substances. — Assuming the solute to be totally dissociated Nernst in 1888[1] derived theoretically an expression for D in terms of the ionic velocities as computed from transference and conductivity data for the case of a salt splitting into two univalent ions. For the more general case in which the salt is completely dissociated into any number of ions of any valence, an expression may be similarly derived,[2] as follows:

Let us take an electrolyte whose formula weight yields on complete dissociation n_c mols of cations of valence v_c and n_a mols of anions of valence v_a. The product of the number of mols of each ion by its valence is necessarily the same for both the positive and negative ions; or $n_c v_c = n_a v_a$. If C is the concentration in formula weights per liter, the number of ions having the same electrical sign is $n_c C$ for the cation and $n_a C$ for the anion; and correspondingly, the concentration-gradients for the cation and anion are $n_c dC/dx$ and $n_a dC/dx$, respectively. As the osmotic pressure of the ions is expressed by $P = nCRT$, the force acting across unit area through the distance dx in the positive direction of x is the difference between the force P at x and $P + dP$ at $x + dx$ or is

$$-n_a RT\frac{dC}{dx}dx \quad \text{and} \quad -n_c RT\frac{dC}{dx}dx$$

for the anions and cations respectively. This is the force that acts upon the ions in the volume dx that is upon $n_a C dx$ and $n_c C dx$ mols of anions and cations so that the force acting upon one mol will be

$$\frac{-n_a RT\frac{dC}{dx}dx}{n_a C dx} = \frac{-n_c RT\frac{dC}{dx}dx}{n_c C dx} = -\frac{RT}{C}\frac{dC}{dx} \qquad (5)$$

it being therefore identical for both the anion and cation.

Now, since the friction against the solvent is different for the different ions one ion would tend to get ahead of the other. This, however, would generate an electrostatic field between the positive and negative ions, which field in turn would accelerate the slower ion and retard the more rapidly moving one. Let us consider the

[1] Loc. cit.

[2] For this derivation I am indebted to Professor A. A. Noyes.

electric potential generated to be E, then the electric force acting upon one mol of cation or anion is $-v_c F \cdot dE/dx$ or $+v_a F \cdot dE/dx$ respectively, where F is one faraday of electricity. The total force acting upon one mol, therefore is:

$$-RT\frac{1}{C}\frac{dC}{dx} - v_c F\frac{dE}{dx} \text{ for the cations,} \tag{6}$$

$$-RT\frac{1}{C}\frac{dC}{dx} + v_a F\frac{dE}{dx} \text{ for the anions.} \tag{7}$$

Let u_c and u_a be the velocities of each ion when the force acting upon one mol is unity, and let dN_c and dN_a be the number of mols of each ion passing a cross-section a in the time dt, then under the above force

$$dN_c = u_c a n_c C\left(-RT\frac{1}{C}\frac{dC}{dx} - v_c F\frac{dE}{dx}\right)dt, \tag{8}$$

$$dN_a = u_a a n_a C\left(-RT\frac{1}{C}\frac{dC}{dx} + v_a F\frac{dE}{dx}\right)dt. \tag{9}$$

But

$$\frac{dN_c}{n_c} = \frac{dN_a}{n_a}, \tag{10}$$

since equivalent quantities of the two ions must pass through any section in the same time, therefore

$$u_c\left(RT\frac{1}{C}\frac{dC}{dx} + v_c F\frac{dE}{dx}\right) = u_a\left(RT\frac{1}{C}\frac{dC}{dx} - v_a F\frac{dE}{dx}\right) \tag{11}$$

or

$$F\frac{dE}{dx} = -\left(\frac{u_c - u_a}{u_c v_c + u_a v_a}\right)\frac{RT}{C}\frac{dC}{dx}. \tag{12}$$

If this value and equation (8) or (9) is substituted in equation (10) above we have

$$\frac{dN_c}{n_c} = dN = -aRT\frac{dC}{dx}\left(\frac{u_a u_c(v_a + v_c)}{u_c v_c + u_a v_a}\right)dt, \tag{13}$$

where dN is the number of formula weights passing cross-section in time dt. If instead of formula weights we use equivalent weights, since one formula weight equals $n_c v_c$ or $n_a v_a$ equivalents, and

$U_c = u_c v_c$ and $U_a = u_a v_a$ represent the velocities when unit-force acts on one equivalent weight of ions we obtain by substitution and reduction

$$dS = - aRT \frac{dc}{dx} \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{v_c} + \frac{1}{v_a} \right) dt, \qquad (14)$$

where dS is the number of equivalents crossing in time dt, and where dc/dx represents the concentration-gradient in equivalents.

By a comparison of this formula with the expession of Fick's law (equation 1) we see that we can express D in terms of quantities derived from electrical measurements or

$$D = RT \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{v_c} + \frac{1}{v_a} \right), \qquad (15)$$

provided, of course, we assume that the solute is totally dissociated, and hence all diffusion is done by the ions only. This condition is approached only in very dilute solutions and hence D is the limiting value at infinite dilution. At other concentrations the value of D as found from Fick's formula will be greater or less according as the undissociated substance diffuses faster or slower than the ions. As a general rule the diffusion constant has been shown to become larger as the dilution is increased and hence we believe that the ions move more rapidly than the undissociated portion.

Diffusion of Partly Ionized Substances. — As shown above, in the case of diffusion of a simple substance, the amount of solute which will diffuse across any plane of cross-section a in the time dt may be expressed by the equation

$$dS = - Da \frac{\partial c}{\partial x} dt.$$

A dissociated solute diffuses in two parts, the dissociated and undissociated, and during an infinitesimal time the parts may be considered as moving independently, each having its own diffusion coefficient.[1] Hence we can say that the total amount crossing the area is equal to the sum of the two parts, that is,

$$dS = dS_1 + dS_2, \qquad (16)$$

[1] Nernst, Z. Phys. Chem., *2*, 634, 1888

where dS_1 and dS_2 represent the number of equivalents of un-ionized substance and of ionized substance, respectively.

$$dS = -D_1 a \frac{\partial c_1}{\partial x} dt - D_2 a \frac{\partial c_2}{\partial x} dt, \tag{17}$$

where c_1 and D_1 refer to the undissociated portions and c_2 and D_2 to the dissociated. As the ions must move together they will not have separate diffusion constants and D_2 will be the constant corresponding to the whole dissociated portion. By reasoning similar to that applied to the general equation we get

$$\frac{\partial c}{\partial t} = \frac{-\frac{\partial (dS)}{\partial x} dx}{a dx} = -\frac{1}{a}\frac{\partial (dS)}{\partial x} = \frac{\partial^2 c_1}{\partial x^2} D_1 + \frac{\partial^2 c_2}{\partial x^2} D_2 + \left(\frac{\partial c_1}{\partial x} D_1 + \frac{\partial c_2}{\partial x} D_2\right)\frac{\partial a}{\partial x}. \tag{18}$$

If the tube is uniform, $\partial a/\partial x = 0$, and we obtain

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2}. \tag{19}$$

Equation (19) is an expression in five variables, of which x and t are independent. It can be considerably simplified with the help of the relation between the concentrations c, c_1 and c_2. Storch[1] and others have found that this relation can be almost exactly expressed between 0.100 normal and zero concentration by an equation of the form $c_1 = Kc_2^n$ (20) where n varies somewhat with the salt but has always approximately the value 1.5. We have also of course $c = c_1 + c_2$.

From these functions we get

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial t}(c_2 + Kc_2^n) = \frac{\partial c_2}{\partial t}(1 + Knc_2^{(n-1)}),$$

$$\frac{\partial c_1}{\partial x} = Knc_2^{(n-1)}\frac{\partial c_2}{\partial x},$$

$$\frac{\partial^2 c_1}{\partial x^2} = Kn\left[c_2^{(n-1)}\frac{\partial^2 c_2}{\partial x^2} + (n-1)c_2^{(n-2)}\left(\frac{\partial c_2}{\partial x}\right)^2\right].$$

[1] Z. Phys. Chem., *19*, 13, 1896.

Substituting these ratios in equation (19) we obtain an expression in c_2, t, and x.

$$(1 + Knc_2^{(n-1)})\frac{\partial c_2}{\partial t^2} = D_2\frac{\partial^2 c^2}{\partial x^2} + D_1\left\{Kn\left[c_2^{(n-1)}\frac{\partial^2 c_2}{\partial x^2} + (n-1)c_2^{(n-2)}\left(\frac{\partial c_2}{\partial x}\right)^2\right]\right\}. \quad (21)$$

If a suitable solution can be found for this equation which will satisfy the conditions of the experiment, the constants D_1 and D_2 could be determined provided we measure the concentrations at various points along the tube at definite times. As yet a method of integrating this equation has not been found, and the equation has therefore been used in its differential form. Empirical expressions can be determined which express the concentration as a function of the distance at the time of each measurement, and also other expressions which express the concentration as a function of the time at the distance of each electrode in the tube. By differentiating these expressions with respect to the distance and time respectively we can obtain differential coefficients which when substituted in the differential equation (21), will give a series of simultaneous equations containing as unknowns D_1 and D_2, the diffusion constants.

Since the concentrations were determined from conductances, as will be described in section 4, it was found more convenient in the experiments to change the dependent variable from c_2 to L, where L is the specific conductance and is equal to the product of c_2 into Λ_0, the equivalent conductance at zero concentration. Making this substitution we obtain as our equation

$$\left[1 + Kn\left(\frac{L}{\Lambda_0}\right)^{n-1}\right]\frac{1}{\Lambda_0}\frac{\partial L}{\partial t} = D_2\frac{1}{\Lambda_0}\frac{\partial^2 L}{\partial x^2} + D_1\left[Kn\left\{\left(\frac{L}{\Lambda_0}\right)^{(n-1)}\frac{1}{\Lambda_0}\frac{\partial^2 L}{\partial x^2} + (n-1)\left(\frac{L}{\Lambda_0}\right)^{(n-2)}\frac{1}{\Lambda_0^2}\left(\frac{\partial L}{\partial x}\right)^2\right\}\right]. \quad (22)$$

This can be reduced to

$$(1 + K_2L^{n-1})\frac{\partial L}{\partial t} = D_2\frac{\partial^2 L}{\partial x^2} + D_1\left[K_2L^{n-1}\left\{\frac{\partial^2 L}{\partial x^2} + (n-1)\frac{1}{L}\left(\frac{\partial L}{\partial x}\right)^2\right\}\right] \quad (23)$$

where

$$K_2 = \frac{Kn}{\Lambda_0^{n-1}}.$$

With this equation if the law expressing the relation between the conductance and concentration of the substance is known and the specific conductances at different points along the tube are measured, the partial derivatives in respect to time and distance at each point and time can be found. Substituting these in the equation above (23) an expression is obtained in which D_2 and D_1 are the only unknowns.

$$P = QD_2 + RD_1. \qquad (24)$$

A number of these expressions found for different times and distances can be combined by applying the method of least squares and the most probable values of D_1 and D_2, the specific diffusion rates can be thereby obtained.

3. WORK OF PREVIOUS INVESTIGATORS.

A large number of articles have been published dealing with the theory of diffusion or with rough quantitative measurements of it. References to these will be found in the footnote.[1] A fuller mention of the recent more exact work of Öholm[2] is however appropriate, since his results for the first time show with some degree of accuracy the effect of integrated concentration intervals on the values of the specific diffusion rates.

His apparatus consisted of a cylindrical tube about 25 cm. long and 3.5 cm. in diameter. Pure water was run in until it filled three fourths of the tube, and under this was run a layer of salt solution of known content. After standing for a time the solution was drawn off at the bottom in four portions and analyzed. By means of the tables of Stefan[3] and Kawalki[4] he calculated the diffusion-constants for varying initial concentrations of his diffusing

[1] Graham, Phil. Trans., 1, 805, 1850; 483, 1851. Fick, Pogg. Ann., *94*, 59, 1855. Simmler and Wild, Pogg. Ann., *100*, 217, 1857. Graham, Phil. Trans., *151*, 183, 1861. Weber, Wied, Ann., 7, 469, 536, 1879. Stefan, Wien. Akad., *79*, 161, 1879. Schaffer, Berichte, *15*, 788, 1882; *16*, 1903, 1883. Nernst, Z. Phys. Chem., *2*, 613. 1888. Voigtlander, Z. Phys. Chem., *3*, 316, 1889. Wiedeburg, Wied. Ann., *41*, 675, 1890. Wiedeburg, Z. Phys. Chem., *10*, 512, 1892. Arrhenius, Z. Phys. Chem., *10*, 51, 1892. Bose, Z. Phys. Chem., *29*, 658, 1899. Wiedeburg, Z. Phys. Chem., *30*, 586, 1899. Graham, Z. Phys. Chem., *50*, 257, 1904. Öholm, Z. Phys. Chem., *50*, 309, 1904,

[2] Öholm, Z. Phys. Chem., *50*, 309, 1904.

[3] Stefan, Wien. Akad., *79*, 161, 1879.

[4] Kawalki, Wied. Ann., *52*, 166, 1894.

solution. He found the same gradation in their values that others had found, and believed it to be mainly due to the change in dissociation, but not entirely, since he found that after a certain concentration was reached the value of the diffusion-constant increased with increasing concentration. This could be accounted for by consideration of Van der Waals' equations. He also came to the conclusion that the temperature-coefficient was equal to the sum of the coefficients of osmotic pressure and electric conductivity, as the kinetic theory requires. By considering measurements of internal friction he came to the conclusion that the internal friction of the molecule was greater than that of the ion, but slightly less than that of the sum of the ions. He also checked Nernst's formula almost exactly.

4. Experimental Method Used in the Investigation.

In order to approach the ideal conditions of diffusion in one direction only, these experiments were carried on in a cylindrical tube held in a vertical position so that the direction of motion of the solute was opposite to the force of gravity. It was found by calculation from known values of diffusion that the force exerted by gravity is negligibly small compared with that exerted by osmotic pressure, and hence as a direct force it would not enter;[1] but if the tube were not perpendicular, as the solute diffused there would be produced by gravity a density-gradient in a direction different from that along the axis of the tube, making measurement uncertain.

[1] As seen in equation (7) the osmotic force acting upon one formula weight of salt is equal to $RT/c \cdot dc/dx$. Assuming the general solution

$$c = c_0\left[1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}du\right] \quad \text{where} \quad u = \frac{x}{2\sqrt{Kt}}$$

and assuming values of K, x and t which will make dc/dx smaller than that found at any place used in our measurements, that is, $K = 1$, $t = 49$, $x = 8$, we obtain

$$\text{Osmotic force} = RT\,\frac{-\frac{1}{14}\cdot\frac{2}{\sqrt{\pi}}e^{-(.57)^2}}{\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{.57} e^{-u^2}du\right]} = 0.12RT = 3 \times 10^9 \text{ dynes.}$$

The force of gravity on one formula weight or 504 grams of Tl_2SO_4 is $504 \times 980 = 4.94 \times 10^5$ dynes; and taking into account the buoyancy of the water the effective force would become considerably less than this.

From the values of the diffusion-constants already determined by other investigators, it was found by calculation, assuming equations (3) and (4), that after three months' time the concentration of solute at a distance of 50 cm. from the foot of the tube would be less than 0.1 per cent. of that at the bottom. Hence within the limits of error of the experiment a tube 50 cm. high would act as if it were infinite in length. The lower end of the tube contained solid salt so that the concentration there was that of the saturated solution, while, by starting with pure water throughout the whole length of the tube, the other end was practically held at zero concentration. To determine the concentrations at different points, pairs of platinized wire electrodes were inserted at definite intervals along the tube and the electrical conductivity between the electrodes of each pair was measured. Each pair was in a plane perpendicular to the axis of diffusion; and the separate wires were near enough together so that the conductivity measured was that corresponding to the concentration at the mean distance of the electrode pair from the lower end of the tube, or from the plane of the solid salt. If the two electrode wires had not been placed near together, as there was a concentration-gradient across each pair which was not linear, the reading would have corresponded to a concentration higher than that present at the mean distance of the wires. In order to ascertain what error was introduced into the calculation by the assumption that the mean distance of the electrode pair was that corresponding to the conductance or concentration measured, an experiment was made in which the upper level of a column of uniformly conducting solution within the tube was lowered until the electrode pair was nearly uncovered. It was found when the upper level of the solution was one millimeter above a pair of wires 4 mm. apart, that the conductance between the wires was about thirty per cent. less than that found when the tube was full. By a calculation assuming formula (4) we see, if $x = 10$, $K = 1$, $t = 25$, and therefore $u = 1.00$ that $c = 0.1574c_0$. If $x = 10.3$ and 9.7 the values of c at those points are $0.1452c_0$ and $0.1701c_0$, respectively. As for such a small change in concentration the rate of change of dissociation with the concentration can be considered a constant, the average of the conductances at the points 10.3 and 9.7 will correspond to the average of their concentrations. This

latter will be $0.1576c_0$ or will correspond to point $x = 9.994$ instead of $x = 10.000$. This would make an error of 0.06 of a millimeter; but, as the distances between the electrodes at the best cannot be determined closer than 0.1 millimeter, this error is negligible. This deviation moreover would be in the same direction for all the electrodes and would in this way tend to eliminate itself in the calculations after the experiment has proceeded for a considerable time, and even more so if the wires were placed nearer together.

It was decided to carry on the experiments in a tube about 50 cm. long and 5 cm. in diameter; but, as it was thought impracticable to insert the electrodes through such a large tube, a smaller one, 1.5 cm. in external diameter, was placed at the axis of the large tube holding the electrodes and containing the lead wires within it. To seal in such large wires as it would be necessary to use would result in protuberances that would cause large deviations in the cross-section of the tube; so holes 3 mm. apart and 1 mm. in diameter, just large enough to pass the wire through, were bored in the small tube by means of a diamond and the whole held firmly in place by filling the small tube with a mixture consisting of 95 per cent. shellac and 5 per cent. ceresin.

This mixture was found the most suitable of several which were tried. Paraffin although the best insulator was not firm enough at 30° to keep the electrodes in place and at that temperature it slowly flowed out between the glass and the electrodes, so covering the latter as to change the cell-constants. No other pure hydrocarbon seemed satisfactory, as none would stick sufficiently to the glass to prevent the formation of an annular space between the glass and the body of the filling material, when the tubes were allowed to cool. Rosin in itself is too brittle; but when mixed with a little paraffin it is still firm and adheres to glass very well, giving fair results. It, however, is slowly attacked by water, thus allowing the solution to work its way into the small tube and around the electrodes and lead wires. Gum shellac seemed to have the best adhesive properties; and, when mixed with about 5 per cent. of a high melting paraffin like ceresin, it sticks firmly to the glass, does not flow, and is attacked very slightly by boiling water. This shellac was prepared from the commercial gum shellac by first dis-

solving it in alcohol, filtering, and then precipitating by adding water to the alcoholic solution. This it was believed would throw down only that portion very insoluble in water. To further obviate, as far as possible, any error which might result from the solubility of the shellac, the precipitate from the alcohol-water solution was boiled repeatedly with conductivity water until a water solution, containing one fourth of its volume of shellac, showed a rise in specific conductance of only 2 or 3×10^{-6} reciprocal ohms after heating for about two or three hours upon a steam bath. As the only shellac surface exposed during a diffusion experiment was that between the wires and the glass, and as, by way of further precaution this space was filled as far as practicable with ceresin, it is believed that very little contamination came from this source.

The electrode wires were one millimeter in diameter and extended about one centimeter beyond the outer surface of the inner tube. The distance between the two wires of a single pair was made about 3.0 mm. The distances between the successive electrode pairs were measured by a cathetometer to 0.1 mm. Although the attempt was made to bore the two holes for a single pair of electrodes in a plane perpendicular to the axis of the tube, this was not always fully successful, so the distance of an electrode pair was taken as the mean distance of upper and lower points of both ends of both wires. This allowed for all deviations in the position of the wires provided they were approximately parallel to each other and perpendicular to the tube. The large outer tubes were calibrated with mercury to determine any deviations in cross-sections; but the variation was so small that it gave rise to an error of less than 0.2 per cent. and was therefore neglected. This small variation was secured by selecting tubes that showed less than 0.1 mm. variation in diameter in 10 cm. length. All tubes were of Jena glass.

For fear that a definite line of saturated solution would not be maintained at the bottom of the tube, holes were bored through the outer tube so that their tops were level with the lowest pair of electrodes. The lower end of the tube was then placed in a beaker containing a saturated solution and a large excess of solid salt above the line of holes, thus keeping by gravity a saturated solution at the line of the lowest electrodes, from which line the distances along

the tube were measured. The top of the beaker was closed air-tight by melting into it a mixture of rosin and paraffin.

The elevation of one of the tubes is shown in Fig. 1.

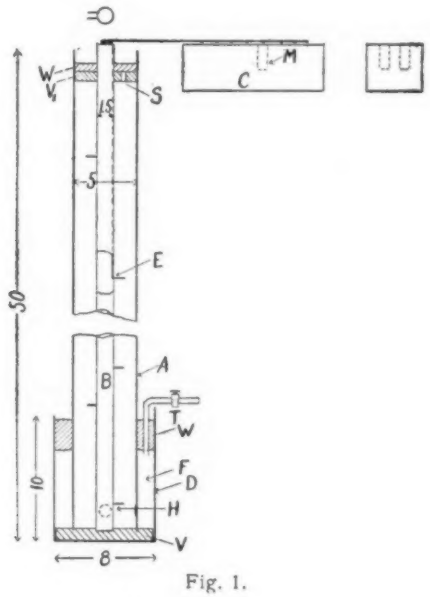

Fig. 1.

A is the outer tube, *B* the inner one containing the electrodes *E*, and *C* a slate block serving as commutator and containing the mercury cups *M* to which the wires lead from the platinum electrodes. *D* is the outside beaker containing the solid salt *F* and saturated solution into which the large outer tube *A* is placed. *H* shows the holes through which the saturated solution flows by gravity keeping a constant concentration at the plane of their tops. *V* and V_1 are vulcanite blocks which hold the two tubes and beaker in their proper positions. *T* is a tube for drawing off the solution at the start, *W* is a filling mixture of shellac or rosin and paraffin, and *S* is a hole in the vulcanite top for the introduction of pure water.

In making up an inner tube the method of procedure is as follows: A Jena glass tube of very uniform diameter equal to about 1.5 cm. and having comparatively thin walls (about 1 mm.) is selected. Pairs of holes 1 mm. in diameter and 3 mm. apart are

bored with a diamond drill at distances approximately 2, 10, 13, 16, 19, 22, 25, and 32 cm. from the end. These distances are purely arbitrary; but the aim is to have them about 3 cm. apart after the second electrode. The last electrode should be so placed that it is in the upper part of the diffusion apparatus, and is used only as a means of determining the extent of any stirring and contamination, because no appreciable amount of salt can reach there by diffusion until about six weeks have elapsed. Platinum wires 1 mm. in diameter and about 2 cm. long are bent at right angles about the middle or a little beyond, and insulated copper wires are soldered to the shorter end. These electrodes and leads are then put in place beginning with the upper pair, by putting the free end of the lead wire through the inner tube until the electrode comes opposite to the hole into which it is desired to place it. It is advisable before cutting the platinum wire to platinize it several times, burning in the black each time in a blast lamp flame. This gives a rough surface and makes the final platinization more satisfactory.

After all the pairs of electrodes are fastened in their proper position on the outside by means of screw clamps, a thick hot alcoholic solution of pure shellac (without ceresin) is run into the tube until the inside of the glass is thus coated with a thin layer of the solution. A current of air is then passed through the tube, evaporating the alcohol and leaving a thin layer of shellac on the inside of the glass and lead wires. This is baked on in a hot closet with frequent passage of air and then the process is repeated several times. By this means a layer of shellac is formed on the glass which does not break away when the tube is cooled. Finally the tube is filled solid with the melted mixture of shellac and ceresin.

The clamps can now be removed and the wires cleaned and platinized. In one of the tubes a coating of iridium black was put on instead of platinum, as it was found to give a much better minimum in making the conductivity measurements; but it is very hard to make the iridium black stick satisfactorily and therefore platinum is preferable.

The wires from the electrodes are led to a commutator block consisting of eight pairs of mercury cups in a block of slate.

The outer tube is ground flat on one end and four holes 1 cm. in

diameter are cut through it in such a manner that when the two tubes are fitted to the vulcanite base, the tops of the holes will be in the same plane as the lower electrode pair of the small tube. The vulcanite top V_1 is also fitted and a hole large enough to pass a glass tube is cut through it.

The two tubes are then put together temporarily, corking the large holes H, and the cell constants of the electrode pairs are determined at 30° with a 0.02 normal solution of potassium chloride or some other solution of known conductance.

In starting an experiment the two tubes are fitted into the block V and into the beaker D as shown in Fig. 1. The lower end of the outer tube up to the lowest electrodes and the beaker about half way up are filled with solid salt. The tube T is put in place and some form of packing, such as a rubber ring, is fitted down upon the salt, then a melted mixture of shellac or rosin and paraffin is poured on top of the packing in order to make the whole air-tight and rigid. Water is added by means of a long tube through S very slowly in order to diminish stirring; and as soon as a point along the tube is reached where the added water shows very low conductance, the solution is drawn off at the tube T, at the same time adding water at the top at an equal speed until the lowest electrodes show only slight conductance. The tube T is then closed, the hole S is corked and a shellac mixture run on top of V_1 to make it tight. The time of starting is taken when the tube T is shut off. The whole is then placed in a thermostat held at 30° and measurements of the conductance at each electrode pair are made every few days. It is better if possible to place the apparatus in the thermostat before completing the drawing off and to have the pure entering water at a little above 30°.

The form and arrangement of the thermostat needs explanation. The first experiment was made with the diffusion apparatus immersed in a large water bath kept at constant temperature by an electric heater and regulator which was easily able to keep the water constant to within 0.02 or 0.03° C. The water level of the bath was kept about 5 cm. below the top of the outer tube, which made it at least 5 cm. above the level of the liquid within the tube. The upper part of the tube B led out through the cover of the

thermostat and the commutator block was placed on top of the cover where it would be dry. The experiment was started; but it was found after a few days that the upper electrodes showed a large conductance and also that they all seemed to have about the same conductance. The first inference was that the solution was being contaminated by the dissolving of the glass, shellac, etc., and much time was spent trying to find some way of making tubes made out of or coated with ceresin work successfully. But these seemed to give the same results and about to the same degree. It was finally discovered that by keeping the lead wires at the same temperature as the thermostat the trouble almost ceased, and therefore that the contamination was due to stirring caused by the conduction of heat by the copper-lead wires from around the inner tube to the outside of the bath, thus producing a denser solution in the region close to the electrodes and causing stirring by gravity. This was obviated by enclosing the lead wires and commutator block in an air space which was also kept at a constant temperature by a regulator and heater. Two successful experiments were carried on in this way, but in the last experiment another form of thermostat was used. This consisted of an air space 60 × 40 × 30 cm. surrounded on five sides with a water jacket 8 cm. in thickness which was kept at constant temperature. The tubes, wires, and block were all placed in this air space and the sixth side was closed with double glass plates separated by 2 cm. of asbestos feathers, and outside of all by two heavy asbestos boards. The air within the space was stirred by a small motor which ran intermittently and the temperature of the surrounding water was kept just enough above 30° (about 30.15°) so that the temperature within was 30.00° + .05. The commutator block was reached by a rod carrying properly spaced lead wires so that after the experiment was started the thermostat did not have to be opened. In this form of thermostat it is to be noted that changes of temperature of the outer bath are taken up so slowly by the air and by the diffusion tubes, since the air has such a low heat-capacity, that large changes of temperature in the outer bath produce no error by stirring in the tubes. On one occasion the heating apparatus failed during the night and the temperature fell about 10°; but no stirring was apparent even after the temperature had been brought back to 30° again.

5. Experimental Data.

Four series of experiments or runs were carried out according to the procedure described in the preceding section. In two of these thallium sulphate and in two barium nitrate was used as the diffusing electrolyte. These salts were chosen because their solubilities were between normal and tenth normal, thus giving concentrations at the electrodes which not only were measurable by means of conductivity, but which also followed the law of Storch.[1] Two runs were started on each substance in order to test the ability of the method to give concordant results. In the second run on each substance the air bath form of thermostat was used in order to eliminate if possible the stirring which was evident in the first experiments. On account of a slight leak in the second tube with barium nitrate the results with it were not satisfactory and are not given below.

In Table I. are given the distances of each pair of electrodes from the bottom and their cell-constants determined both before and after each run. These cell-constants were determined by measuring in the tube at 30° a 0.02000 normal potassium chloride solution made up at 18°. The value of the specific conductance of potassium chloride was taken as 0.003036 reciprocal ohms.

In Tables II., III. and IV. are given the actual conductances during the diffusion experiments measured at the different electrodes at the times indicated. The times are expressed in days and fractions of a day. The electrode distances are in centimeters.

In order to determine what correction must be applied to the actual conductance on account of the contamination to the solution from the glass, electrodes, shellac, etc., a blank run was made for two months using conductivity water. The increase in specific conductance in 30 days was found to be about 6 to 8×10^{-6} reciprocal ohms. This value did not seem to increase much for the next 30 days. In the first thallium sulphate run no attempt was made to correct for the slight stirring which apparently occurred because it was impossible to tell how far down the tube it extended. In the second run between the times 4.29 and 7.25 the thermostat had to be opened and some stirring resulted. In this case it was

[1] Loc. cit.

corrected for because it seemed to be uniform along the whole tube. In Table V. the corrections applied to the specific conductance are given and in Tables VI., VII. and VIII. are given the final corrected values of specific conductance used in the calculations.

In order to determine the constants in the concentration law $c_1 = Kc_2^n$, series of measurements of conductance were made upon the two salts at 30°.

If for c_1 and c_2 are substituted their values,

$$c_1 = L\left(\frac{1}{\Lambda} - \frac{1}{\Lambda_0}\right) \quad \text{and} \quad c_2 = \frac{L}{\Lambda},$$

the above expression changes to

$$\frac{1}{\Lambda} - \frac{1}{\Lambda_0} = \frac{K}{\Lambda_0^n}(L)^{n-1}$$

in which L and Λ are the specific and equivalent conductances at corresponding concentrations, Λ_0 the equivalent conductance at zero concentration and K and n empirical constants. By applying the following conductance values to this equation and solving several simultaneously not only were K and n calculated but also Λ_0. This seems to be the best method to determine Λ_0 as the solutions used are dilute and the law holds to as great dilution as measurements can be made accurately.

Concentration.	Tl_2SO_4.		$Ba(NO_3)_2$	
	Λ Found.	Λ Calc.	Λ Found.	Λ Calc.
0.8550[1]			61.8	67.1
0.2458[2]	90.7	87.7		
0.1000	104.8	104.6	100.6	100.6
0.0500	116.9	117.3	110.3	110.4
0.02000	132.4	132.4	121.6	121.7
0.01000	142.3	142.2	128.0	128.6
0.004000	152.4	152.4	135.8	135.6
0.002000	158.4	158.2	139.4	139.4
Λ_0		173.4		149.8
n		1.55		1.53
K		3.079		2.052

[1] Sat. Sol. $Ba(NO_3)_2$. [2] Sat. Sol. Tl_2SO_4.

TABLE I.

Values of Cell Constants. Thallium Sulphate. Run No. 1.

Electrode Distance.	8.28	11.40	14.25	17.31	20.29	23.21	33.25
Cell Constant before Run	1.092	0.9738	1.044	0.8774	0.9137	0.9007	0.7504
After Run	1.101	0.9795	1.043	0.8788	0.9124	0.9000	0.7511

Thallium Sulphate. Run No. 2.

Electrode Distance.	11.13	13.98	17.04	20.02	22.94	32.98
Cell Constant before Run	0.9694	1.035	0.8718	0.9097	0.9001	0.7501
After Run	0.9743	1.038	0.8748	0.9099	0.8991	0.7543

Barium Nitrate. Run No 1.

Electrode Distance.	8.52	11.63	14.69	17.80	20.78	30.80
Cell Constant before Run	1.003	0.9160	0.9162	0.7554	0.8778	0.9346
After Run	1.007	0.9111	0.9166	0.7571	0.8758	0.9404

TABLE II.

Thallium Sulphate. Run No. 1. *Values of Actual Conductance. Reciprocal Ohms* $\times 10^6$.

Time.	Electrode Distance.						
	8.28	11.40	14.25	17.31	20.29	23.21	33.25
0.00	12	14	10	6	4	4	3
2.00	30	15	11	7	5	6	4
4.88	641	80	12	7	5	6	5
8.00	1,882	476	82	15	8	8	7
14.00	4,454	1,821	585	181	24	19	17
17.67	5,186	2,702	1,064	432	115	27	22
20.84	5,998	3,427	1,509	711	223	41	41
24.87	6,798	4,251	2,080	1,119	429	140	58
27.72	7,340	4,817	2,493	1,433	594	217	74
30.75	7,796	5,334	2,896	1,739	799	353	87
33.61	8,206	5,795	3,273	2,107	1,009	471	132
36.11	8,513	6,169	3,587	2,405	1,199	583	149
38.89	8,890	6,594	3,936	2,726	1,418	729	169
42.06	9,219	6,988	4,296	3,080	1,672	912	209
45.07	9,515	7,358	4,625	3,409	1,914	1,083	250
48.13	9,811	7,725	4,952	3,745	2,168	1,268	342
51.07	10,010	8,004	5,222	4,033	2,392	1,431	365
52.71	10,210	8,230	5,406	4,219	2,533	1,536	390

TABLE III.

Thalium Sulphate. Run No. 2. Values of Actual Conductances. Reciprocal Ohms $\times 10^6$.

Time, Days.	Electrode Distance.					
	11.13	13.98	17.04	20.02	22.94	32.98
0.00	23	13	10	5	7	5
4.29	81	16	15	10	13	12
7.25	314	30	34	27	29	32
10.24	942	206	48	31	32	35
16.25	2,393	873	346	88	38	43
22.08	3,730	1,693	863	306	116	50
27.26	4,798	2,444	1,435	599	262	59
31.02	5,448	2,954	1,864	852	405	68
36.07	6,258	3,624	2,471	1,237	644	80
41.32	6,977	4,232	3,061	1,646	920	97
46.38	7,593	4,809	3,633	2,063	1,223	149
50.00	7,986	5,176	4,022	2,357	1,445	205

TABLE IV.

Barium Nitrate. Run No. 1. Values of Actual Conductance. Reciprocal Ohms $\times 10^6$.

Time.	Electrode Distance.					
	8.52	11.63	14.69	17.80	20.78	30.80
0.00	18	22	8	7	6	4
3.06	225	37	23	26	13	10
6.75	2,716	446	72	41	22	17
9.91	5,825	1,552	312	48	29	23
13.95	9,450	3,695	1,022	267	55	35
17.19	11,960	5,391	1,859	593	122	47
19.83	13,820	6,913	2,711	1,041	259	56
22.75	15,610	8,482	3,687	1,622	443	81
25.15	16,850	9,694	4,522	2,171	664	92
27.93	18,230	11,080	5,495	2,867	977	108
30.90	19,530	12,430	6,539	3,659	1,352	135
34.00	20,690	13,750	7,602	4,533	1,793	169
37.06	21,850	14,990	8,644	5,428	2,273	256

The unit of concentration was taken one equivalent per liter. The values of Λ must therefore be divided by 1,000 when used in the equations. The values given in columns 2 and 4 are the means of several independent determinations which agreed among them-

TABLE V.

Correction to Specific Conductances for Initial Conductance and Contamination. Reciprocal Ohm $\times 10^6$. *Thallium Sulphate. Run No.* 1.

Electrode Distance.	8.28	11.40	14.25	17.31	20.29	23.21	33.25
After 25 days	15	16	13	10	8	8	7
After 50 days	19	20	17	14	12	12	12

Thallium Sulphate. Run No. 2.

Electrode Distance.	11.13	13.98	17.04	20.01	22.94	32.98
After 20 days	31	27	28	26	27	25
After 50 days	33	29	30	28	29	27

Barium Nitrate. Run No. 1.

Electrode Distance.	8.52	11.63	14.69	17.80	20.78	30.80
After 20 days	36	32	16	10	8	6
After 40 days	45	34	18	12	10	8

TABLE VI.

Thallium Sulphate. Run No. 1. *Corrected Values of Specific Conductances. Reciprocal Ohms* $\times 10^6$.

Time.	Electrode Distance.						
	8.28	11.40	14.25	17.31	20.29	23.21	33.25
0.00	0	0	0	0	0	0	0
2.00	20	11	0	0	0	0	0
4.88	688	64	2	0	0	0	0
8.00	2,043	448	74	6	1	0	0
14.00	4,853	1,758	598	11	9	6	5
17.67	5,652	2,616	1,100	370	98	23	9
20.84	6,540	3,322	1,563	615	197	30	25
24.87	7,439	4,136	2,158	972	383	118	37
27.72	8,037	4,690	2,589	1,249	535	188	49
30.75	8,542	5,196	3,010	1,517	722	310	58
33.61	8,996	5,648	3,403	1,839	913	415	92
36.11	9,334	6,015	3,730	2,101	1,086	516	104
38.89	9,750	6,431	4,094	2,383	1,286	647	119
42.06	10,118	6,819	4,469	2,693	1,517	811	148
45.07	10,446	7,183	4,812	2,981	1,739	965	179
48.13	10,770	7,542	5,153	3,277	1,969	1,130	247
51.07	11,000	7,819	5,434	3,529	2,174	1,277	264
52.71	11,220	8,041	5,626	3,691	2,301	1,377	281

TABLE VII.

Thallium Sulphate. Run No. 2. Corrected Value of Specific Conductance. Reciprocal Ohms $\times 10^6$.

Time.	Electrode Distance.					
	11.13	13.98	17.04	20.02	22.94	32.98
0.00	0	0	0	0	0	0
4.29	52	0	0	0	0	0
7.25	274	5	2	2	2	2
10.24	883	186	15	3	3	3
16.25	2,290	878	274	56	8	8
22.08	3,595	1,728	726	252	78	13
27.26	4,635	2,505	1,224	519	209	20
31.02	5,265	3,032	1,599	748	336	25
36.07	6,052	3,727	2,128	1,099	551	34
41.32	6,751	4,354	2,643	1,470	799	46
46.38	7,349	4,953	3,141	1,849	1,071	85
50.00	7,731	5,333	3,481	2,117	1,281	128

TABLE VIII.

Barium Nitrate. Run No. 1. Corrected Values of Specific Conductance. Reciprocal Ohms $\times 10^6$.

Time.	Electrode Distance.					
	8.52	11.63	14.69	17.80	20.78	30.80
0.00	0	0	0	0	0	0
3.06	203	10	7	2	2	2
6.75	2,706	374	54	20	9	8
9.91	5,832	1,390	271	27	17	14
13.95	9,510	3,254	921	192	40	27
17.19	12,040	4,893	1,687	438	99	39
19.83	13,880	6,284	2,468	778	219	49
22.75	15,670	7,713	3,363	1,217	380	71
25.15	16,920	8,814	4,127	1,632	573	80
27.93	18,310	10,067	5,020	2,158	847	95
30.90	19,620	11,296	5,976	2,757	1,174	119
34.00	20,800	12,526	6,950	3,420	1,560	151
37.06	21,970	13,630	7,905	4,098	1,980	233

selves to 0.1 per cent. The values in columns 3 and 5 are those calculated from the values of Λ_0, n, and K given and are seen to correspond closely to those found for all values between 0.10 normal and zero concentration but do not correspond for the saturated solution. As the equation is used only in its differential form, and

the diffusion values are computed by means of concentrations between 0.2 and 0.01 normal, it is not necessary that the formula should hold beyond that range; but as the value of Λ_0 serves to determine the dissociation we have made our formula correspond more exactly to the values for the dilute solutions than to those for the more concentrated ones.

6. Calculation of Diffusion Constants.

In equation (23) the unknown quantities are the two constants D_1 and D_2 and the three variables $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$. These variables are to be determined empirically from our measurements for each time at each electrode along the tube. An attempt was made to do this graphically, but the errors that would arise in getting a second derivative by plotting were too great; so they were determined analytically. In doing this, it was found most convenient to obtain empirical expressions for each time of measurement which would include all electrode-distances, and expressions for each electrode-distance which would include all times. By differentiating these expressions the derivatives $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$ for each time at each electrode were obtained. The form of expression found to be most satisfactory was

$$L = L_0\left[1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}du\right], \qquad (25)$$

where

L = specific conductance at any point x and any time t,

L_0 = specific conductance calculated to correspond to the point $x = 0$, which is nearly that of the saturated solution.

$$u = \gamma + \frac{\alpha + \beta x}{t}. \qquad (26)$$

α, β, and γ are empirical constants found by trial to satisfy equation (25)

x = distance above the level of the saturated solution.

t = time of diffusion.

In the equation (25) the value of L_0 is not the actual value of the specific conductance in the saturated solution, but is the conductance which a saturated solution would have if the formula $c_1 = Kc_2^n$

held over the whole range. It is therefore in reality nothing more than an additional empirical constant.

When the separate expressions were computed for thallium sulphate, it was found that a general expression of similar form could be made which would satisfy all the conductance values. In fact this expression could be reduced to equation (25) where

$$u = \frac{\beta x}{\sqrt{t}} \tag{27}$$

or

$$u = \gamma + \frac{\beta x'}{\sqrt{t}}, \tag{28}$$

and the values of L computed from this formula checked those measured with an average deviation less than 0.2 per cent. In the second run on thallium sulphate (27) was used, while in the first run (28)[1] was used, although an expression similar to (27) satisfied the values of L almost as closely. In the barium nitrate run the check was not so good and deviations as much as 0.8 per cent. were apparent at the electrode at the distance 8.52. This is not surprising because the conductance values of barium nitrate may have some doubt cast upon them from the fact that on some of the electrodes after the diffusion there was found to be some plant growth. This may have influenced the cell constant values, as it would naturally have become dislodged when the tube was cleaned and the cell constants redetermined. Yet the values of diffusion-constants cannot be effected more than a few per cent. when a mean of all the values is taken.

The values of γ and β are as follows:

	Tl_2SO_4		$BaNo_3$	
	γ	β	γ	β
First Run	0.0181	0.4129	0	0.4358
Second Run	0	0.4128		
L_0	0.02155		0.05735	

By the help of equation (25), our general differential equation (25) can be somewhat simplified by finding expressions for

[1] Equation (28) is the same as (26) as the expression $\alpha + \beta x$ can be put in the form x' by adding a constant quantity to each value of x.

$$\frac{\partial L}{\partial t}, \quad \frac{\partial L}{\partial x}, \quad \frac{\partial^2 L}{\partial x^2},$$

$$\frac{\partial L}{\partial t} = L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u}\frac{\partial u}{\partial t}\right] = L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u^2}\frac{\beta x}{t^{\frac{3}{2}}}\left(-\tfrac{1}{2}\right)\right] = \frac{L_0}{\sqrt{\pi}}e^{-u^2}\frac{\beta x}{t^{\frac{3}{2}}},$$

$$\frac{\partial L}{\partial x} = L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u}\frac{\partial u}{\partial x}\right] = L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u^2}\frac{\beta}{\sqrt{t}}\right],$$

$$\frac{\partial^2 L}{\partial x^2} = L_0\left[-\frac{2}{\sqrt{\pi}}\frac{\beta}{\sqrt{t}}e^{-u^2}(-2u)\frac{\partial u}{\partial x}\right] = L_0\left[\frac{4}{\sqrt{\pi}}\frac{\beta^2}{t}e^{-u^2}u\right].$$

Substituting these values in equation (25) we obtain as our working equation

$$\frac{(K_2L^{n-1}+1)x}{4\beta\sqrt{t}} = uD_2 + D_1(K_2L^{n-1})\left[u + \frac{(n-1)}{\sqrt{\pi}}\left(\frac{L_0}{L}e^{-u^2}\right)\right]. \quad (31)$$

All the quantities in this equation are either known or can be computed from the data except D_1 and D_2; hence we can write

$$P = QD_2 + RD_1, \quad (26)$$

$$P = \frac{(K_2L^{n-1}+1)x}{4\beta\sqrt{t}},$$

TABLE IX.

Values of P, Q and R for Thallium Sulphate. Run No. 1.

Values of P.

Time, Days.	Electrode Distance.				
	8.28	11.40	14.25	17.31	20.29
24.87	1.854	2.230	2.469	2.680	
27.72	1.789	2.168	2.411	2.617	
30.75	1.726	2.106	2.353	2.554	
33.61	1.674	2.053	2.303	2.513	2.685
36.11	1.632	2.010	2.264	2.477	2.645
38.89	1.592	1.969	2.223	2.438	2.605
42.06	1.545	1.920	2.178	2.395	2.563
45.07	1.505	1.878	2.137	2.356	2.525
48.13	1.469	1.840	2.100	2.320	2.491
51.07	1.435	1.803	2.064	2.287	2.459
52.71	1.421	1.787	2.047	2.271	2.443

Values of $Q = u$.

24.87	0.6675	0.9226	1.1627	1.4169	
27.72	0.6299	0.8717	1.0991	1.3408	
30.75	0.5995	0.8287	1.0444	1.2793	
33.61	0.5732	0.7930	0.9984	1.2166	1.4350
36.11	0.5542	0.7652	0.9633	1.1718	1.3834
38.89	0.5312	0.7352	0.9267	1.1282	1.3317
42.06	0.5115	0.7085	0.8915	1.0848	1.2793
45.07	0.4940	0.6839	0.8612	1.0481	1.2351
48.13	0.4770	0.6609	0.8323	1.0127	1.1935
51.07	0.4653	0.6433	0.8097	0.9846	1.1600
52.71	0.4541	0.6295	0.7947	0.9674	1.1404

Values of R.

24.87	1.0500	0.9858	0.8399	0.6430	
27.72	1.0480	0.9979	0.8835	0.7052	
30.75	1.0440	1.0230	0.9191	0.7525	
33.61	1.0390	1.0330	0.9462	0.8002	0.6311
36.11	1.0340	1.0400	0.9658	0.8332	0.6713
38.89	1.0270	1.0450	0.9847	0.8644	0.7122
42.06	1.0210	1.0470	1.0000	0.8958	0.7526
45.07	1.0140	1.0500	1.0120	0.9175	0.7865
48.13	1.0060	1.0500	1.0220	0.9389	0.8175
51.07	0.9998	1.0490	1.0280	0.9541	0.8416
52.71	0.9917	1.0480	1.0330	0.9638	0.8553

$$Q = u,$$

$$R = (K_2 L^{n-1})\left(u + \frac{n-1}{\sqrt{\pi}}\frac{L_0}{L}e^{-u^2}\right),$$

$$K_2 = \frac{Kn}{A_0^{n-1}}.$$

TABLE X.

Values of P, Q and R. Thallium Sulphate. Run No. 2.

Values of P.

Time, Days.	Electrode Distance.			
	11.13	13.98	17.04	20.02
22.08	2.246	2.484	2.711	2.918
27.26	2.131	2.374	2.595	2.775
31.02	2.054	2.303	2.523	2.696
36.07	1.967	2.224	2.446	2.614
41.32	1.888	2.146	2.372	2.538
46.38	1.820	2.083	2.311	2.478
50.00	1.775	2.039	2.271	2.440

Values of $Q = u$.

22.08	0.9777	1.2370	1.5018	1.7830
27.26	0.8766	1.1108	1.3470	1.5952
31.02	0.8233	1.0417	1.2625	1.4933
36.07	0.7626	0.9636	1.1674	1.3800
41.32	0.7130	0.9022	1.0915	1.2896
46.38	0.6733	0.8490	1.0288	1.2149
50.00	0.6489	0.8178	0.9895	1.1692

Values of R.

22.08	0.9583	0.7850	0.5794	0.3791
27.26	1.006	0.8754	0.7001	0.5087
31.02	1.025	0.9208	0.7658	0.5859
36.07	1.040	0.9656	0.8362	0.6683
41.32	1.047	0.9954	0.8892	0.8720
46.38	1.050	1.0160	0.9292	0.8015
50.00	1.049	1.0270	0.9517	0.8349

An equation of the form of the above was found for each time at each electrode and the values of P, Q, and R computed are given in Tables IX., X. and XI.

TABLE XI.

Values of P, Q and R for Barium Nitrate. Run No. 1.

Values of P.

Time, Days.	Electrode Distance.			
	8.52	11.63	14.69	17.80
19.83	2.074	2.374	2.565	
22.75	1.996	2.311	2.508	
25.15	1.937	2.260	2.466	
27.93	1.877	2.210	2.422	2.572
30.90	1.819	2.158	2.379	2.530
34.00	1.762	2.108	2.335	2.492
37.06	1.714	2.062	2.298	2.459

Values of $Q = u$.

19.83	0.8272	1.1314	1.4308	
22.75	0.7746	1.0583	1.3372	
25.15	0.7405	1.0087	1.2724	
27.93	0.7042	0.9580	1.2082	1.4697
30.90	0.6716	0.9123	1.1490	1.3980
34.00	0.6436	0.8703	1.0958	1.3319
37.06	0.6168	0.8349	1.0493	1.2745

Values of R.

19.83	1.290	1.105	0.8297	
22.75	1.305	1.162	0.9194	
25.15	1.311	1.198	0.9804	
27.93	1.313	1.229	1.0390	0.7916
30.90	1.313	1.260	1.0900	0.8606
34.00	1.310	1.275	1.133	0.9243
37.06	1.302	1.288	1.169	0.9781

The large number of equations of form (24) corresponding to these values of P, Q and R were then solved for D_1 and D_2 by combining them in accordance with the method of least squares.

In this treatment our equations would be as follows, where V is the probable deviation :

$$P - QD_2 - RD_1 = V,$$

$$V_1 \frac{\partial V_1}{\partial D_2} + V_2 \frac{\partial V_2}{\partial D_2} = \Sigma V \frac{\partial V}{\partial D_2} = 0. \tag{30}$$

Similarly

$$\Sigma V \frac{\partial V}{\partial D_1} = 0. \tag{31}$$

Solving these

$$\Sigma PQ - D_2 \Sigma Q^2 - D_1 \Sigma QR = 0, \tag{32}$$

$$\Sigma PR - D_2 \Sigma QR - D_1 \Sigma R^2 = 0. \tag{33}$$

The numerical values of these two latter expressions are

Tl_2SO_4 Run 1.

$$106.606 = 47.250 D_2 + 42.725 D_1$$
$$102.187 = 42.725 D_2 + 46.200 D_1$$
$$D_1 = 0.765$$
$$D_2 = 1.563$$

Tl_2SO_4 Run 2.

$$73.825 = 35.967 D_2 + 24.844 D_1$$
$$54.382 = 24.844 D_2 + 27.412 D_1$$
$$D_1 = 0.797$$
$$D_2 = 1.503$$

$Ba(NO_3)_2$ Run 1.

$$59.045 = 28.244 D_2 + 28.184 D_1$$
$$62.223 = 28.184 D_2 + 32.923 D_1$$
$$D_1 = 0.688$$
$$D_2 = 1.404$$

7. Discussion of the Results.

The probable error of D_1 and D_2 as determined from the preceding equations by the method of least squares assuming equal weights for all values is 0.5 per cent. This low value, however, cannot be cited as a measure of the accuracy of the two constants for it does not take into account any constant errors or those that may be caused by inexact assumptions.

In order to give an idea as to the direction and magnitude of the possible variations in the diffusion constants, combinations have been made of some of the different single equations (24) from which the final mean was derived. For this purpose Tl_2SO_4, run no. 2 was taken and values calculated for different pairs of electrode distances and at different times. In the following table are shown the values of D_1 and D_2 calculated, using the same intervals of electrode distances and changing the time and also using the same time interval but taking values at different distances.

Times.	Distance Interval, 11.13 to 17.04.		Distance Interval, 13.98 to 20.02.		Electrode Distance.	Time Interval, 27.26 to 50.00.	
	D_1	D_2	D_1	D_2		D_1	D_2
27.26	1.508	0.804	1.470	0.846	11.13	1.690	0.647
36.07	1.562	0.750	1.507	0.801	13.98	1.535	0.762
50.00	1.646	0.673	1.552	0.752	17.04	1.492	0.835
					20.02	1.461	0.879

From the above values it is seen that the variations in values of D_1 and D_2 are regular and not of such a character as could be claimed to be due to accidental errors. In this connection it is also noticeable that D_1 and D_2 computed from the two different runs of Tl_2SO_4 differ by about 4 per cent. and yet the values of conductance at the corresponding electrodes differ but very little from each other. If in the first run the values at the first electrode are not considered it is found that the values of the diffusion-constants fall near to those in run no. 2. This is practically reducing the calculation to electrodes at the same distances from the end and would seem to indicate that the trouble is theoretical in the assumptions. This is also indicated by the fact that when the first

electrode of the barium nitrate tube is not used, the values of the constant of the ion is reduced to about 1.37.

What the cause of these variations may be is uncertain, but there are many possibilities. The salts may dissociate in steps into intermediate ions like $TlSO_4$ and Tl. The mobilities of the ions may change with dilution. The ions and undissociated portion may not diffuse independently having a dragging influence one upon the other. But in any case the effect is not large, amounting to a few per cent. only.

Another fact worthy of mention is that no matter whether the diffusion constants are calculated using a few electrode distances and times or all of them, it is always true of the different pairs of values that the sum of the two diffusion constants of any one salt is a constant. No explanation of this presents itself.

It is of interest to see what values are obtained for the different diffusion constants of the ions alone by the consideration of formula (15) derived on page 151. When numerical values are inserted in this formula[1] we obtain for thallium sulphate and barium nitrate, respectively,

$$D_2 = 0.02243 \frac{84.9 \times 88.4}{173.3} \frac{3}{2} (1.041) = 1.517,$$

$$D_2 = 0.02243 \frac{72.42 \times 77.38}{149.8} \frac{3}{2} (1.041) = 1.310.$$

These are seen to be lower than the experimentally found ones for the first thallium sulphate run and for the barium nitrate one but about the same for the second thallium sulphate run. This is probably due to the fact that this latter run was calculated using more dilute solutions than the first and would in consequence come nearer to satisfying the theory than the first in which the fairly concentrated solutions at the electrode distance 8.28 were brought into the calculations.

Another calculation seems worthy of mention. It was found that the values of L in formulas (27) and (29) are very nearly satisfied when $\beta = 0.4129$ and $\beta = 0.4358$ for thallium sulphate and barium

[1] See Nernst, Theoret. Chemie, 4th ed., p. 367.

nitrate, respectively. Now according to equations (5) and (6) if there were no undissociated portion

$$\beta = \frac{1}{2\sqrt{D_2}}.$$

This would also hold true provided ions are never transformed into or produced out of un-ionized molecules, since in that case the total concentration of the ions at any point is simply determined by the quantity of them that have diffused as such to that point. If a calculation is made in this way the values of D_2 are found to be *1.468* and *1.316* for thallium sulphate and barium nitrate respectively. These, it is seen, are very close to the value calculated from the equivalent conductances of the ions by Nernst equation (16) which were *1.517* and *1.310* respectively. This agreement shows that the assumption just stated in regard to the non-transformation of ionized and un-ionized substance is at least approximately fulfilled, and therefore that the ions and un-ionized molecules must diffuse at such relative rates as will make transformation unnecessary. Namely, between the quantities dN_1 and dN_2 of un-ionized and ionized substance passing a given cross-section in time dt, there must evidently exist the relation $dN_1/dN_2 = C_1/C_2$, if there is to be no transformation in the adjoining cross-section. Now under the assumption of the independent diffusion of the two forms of the salt, which has been made throughout this article, it is easy to determine the corresponding relation which must exist between the specific diffusion-rates D_1 and D_2 of the un-ionized and ionized substance. Namely, since

$$dN_1 = -D_1 \frac{\partial c_1}{\partial x} dt \quad \text{and} \quad dN_2 = -D_2 \frac{\partial c_2}{\partial x} dt,$$

it follows by division of the first of these equations by the second and combination of the result with the preceding equation that

$$\frac{D_1}{D_2} \frac{(\partial c_1/\partial x)}{(\partial c_2/\partial x)} = \frac{c_1}{c_2} \quad \text{or} \quad \frac{D_1}{D_2} = \frac{\partial \log c_2/\partial x}{\partial \log c_1/\partial x}.$$

Combining this result with the concentration-function expressed by the equation $c_1 = Kc_2^n$ from which follows:

$$\log c_1 = n \log c_2 + \log K \quad \text{and} \quad d \log c_1 = n d \log c_2,$$

we get $D_1 = D_2/n$. And in fact this relation is not very far from being fulfilled.

So far the probability of theoretical errors existing in the method has been discussed, but before concluding that the deviations must be principally due to that source it will be well to examine into the possibility of experimental errors. The fact that a low "probable error" of 0.5 per cent. was obtained only indicates that equation (25) satisfies the data and that such accidental errors as our likely to occur would make small deviations in the final mean. This takes no account however of the constant errors which would not tend to eliminate each other in the computation of the mean and would thus give incorrect values to it.

Five classes of quantities were measured during the experiments: the distances between the electrodes, the cell-constants, the conductances at each electrode, the time of each measurement of conductance, and the temperatures both at these times and during the rest of the experiment. Besides these, measurements were made by which the concentration-function of each electrolyte was determined; but these were carried on according to the usual Kohlrausch methods for determining conductance, and the checks that were obtained showed a precision of 0.1 to 0.2 per cent. in the values of conductance. Moreover, the values of conductance computed by the concentation-function checked those experimentally found within 0.1 per cent.

Without entering here into a discussion of the effect of errors in these measured quantities on the values of the diffusion constants, it may be stated that such a consideration shows that the possible error in each of these measured quantities can hardly give rise to an error of more than 0.2–0.3 per cent. in the final values of D_2, the diffusion-constant for the ions, so that the combined effect of all these errors is not likely to exceed 0.5 per cent. A far more important source of error is that arising from a slight convection which seems to have been due to minute temperature differences, such as were caused in one run by the fact that the lead wires were sometimes under a slightly different temperature from that of the bath, and in another by the fact that one side of the air bath was not kept at exactly the same temperature as the rest of it. This

stirring was indicated by the fact that more salt reached the upper part of the tube as shown greater conductances, when such changes of temperature were known to exist than when the temperature was known to be constant throughout. A comparison of the two runs with thallium sulphate made under dissimilar conditions and showing quite different concentrations at the upper electrode leads to the belief that there may be an error of 2 or 3 per cent. from this source; but, as it is not known whether it is positive or negative and there are indications that it may have a different sign at different points, the probabilities are that the final mean values will be in error by a smaller per cent. In view of this experimental error it is believed that the precision of final values of D_2, so far as the experimental part of the determination is concerned, can be placed at 2 per cent. If the trouble from stirring can be eliminated a precision of 0.5 per cent. in the method can be expected so far as experimental errors are concerned.

8. Summary and Conclusion.

In the foregoing pages has been described a method for the direct determination of the specific diffusion rates or diffusion constants of both the undissociated and the dissociated portion of partly ionized substances. The method consists in allowing the salt to diffuse upwards into a long cylindrical tube initially filled with pure water, keeping the concentration constant at the lower end. The concentration of the electrolyte is determined at different times and at different points along the tube by measuring the electrical conductance between platinum wires arranged in pairs and placed at different distances along the tube. Three runs were made, two in which thallium sulphate and one in which barium nitrate was used as the diffusing substance.

The principles involved in the calculations are as follows: Assuming that Fick's law of diffusion

$$dS = -Da\frac{\partial c}{\partial x}dt$$

applies both for the ionized and un-ionized portions, that is, assuming that the diffusion of the ions and undissociated portions takes place independently, the following differential equation has been derived

which expresses the changes in the concentrations in this tube with respect to the time and the distance along the tube.

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2},$$

where

c = total concentration in equivalents per cubic centimeter,
c_1 = concentration of undissociated portion,
c_2 = " " dissociated "
x = distance in centimeters along the tube from the plane of constant concentration.
t = time in days during which the diffusion has been progressing.
D_1 and D_2 = diffusion constants for the undissociated and dissociated portion respectively.

By means of the empirical relations which exist between the total concentration and those of the ionized and un-ionized portions

$$c = c_1 + c_2, \quad c_1 = Kc_2^n,$$

in which K and n are empirical constants, the above equation is simplified to the following one involving only one independent variable c_2,

$$(1 + Knc_2^{n-1}) \frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} + D_1 \left[(Knc_2^{n-1}) \left\{ \frac{\partial^2 c_2}{\partial x^2} + (n-1) c_2^{n-2} \left(\frac{\partial c_2}{\partial x} \right)^2 \right\} \right].$$

As it was found impossible to integrate this equation it was necessary to determine c_2 and the differential coefficient $\partial c_2/\partial t$, $\partial c_2/\partial x$, $\partial^2 c_2/\partial x^2$ for different points along the tube at different times and thus to obtain expressions containing only D_1 and D_2. In order to facilitate the calculations, advantage was taken of the fact that the concentration c_2 is proportional to the specific conductance L and that the ratio of the equivalent conductance at any concentration to that at zero concentration is a measure of the dissociation. This enables the last equation to be changed into one in which the only variable quantities are the values of L and those of the three differential

coefficients $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$. These values of L and those of the differential coefficients were determined from the conductance measurements and equations were thus obtained for various times and distances in which the only unknowns are D_1 and D_2. By solving the large number of these equations simultaneously by the method of least squares, the best values of D_1 and D_2 were calculated. These were found for thallium sulphate and barium nitrate to be

Salt.	Run.	D_1	D_2
Tl_2SO_4	1	0.77	1.56
	2	0.80	1.50
$Ba(NO_3)_2$	1	0.69	1.40

From these values it is seen that the rate of diffusion of the undissociated substance is one half that of the ionized portion. This shows that the friction encountered by the molecule is twice the average of that encountered by the two ions which is in all probability due to the larger size of the former.

In a manner similar to that used by Nernst[1] an equation has been derived in which D_2, the diffusion constant of the ionized portion for any salt dissociated into more than two ions of any valence, can be calculated from the equivalent conductance values of the ions at great dilution. This equation is

$$D_2 = KRT \frac{U_a U_c}{U_a + U_c}\left(\frac{1}{V_a} + \frac{1}{V_c}\right).$$

U_a and U_c = equivalent conductances in reciprocal ohms of anion and cation at great dilution.

V_a and V_c = valences of anion and cation.

K = constant depending on units used which has the value $9.854 + 10^{-13}$ when R is expressed in ergs per centigrade degree, and D_2 in equivalents per day.

The values of D_2 calculated by means of this latter formula are 1.52 and 1.31 for thallium sulphate and barium nitrate, respectively. These values are seen to correspond closely to those found by means of our measurements and are a confirmation of the results

[1] Z. Phys. Chem., *2*, 613, 1888.

of the diffusion experiments and of the assumptions involved in the calculations, especially that the ions and un-ionized molecules diffuse independently and that the ionization is given at least approximately by the conductance ratio.

If instead of using the differential equation

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2}$$

it is assumed that the equation

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2}$$

is applicable, the value of D_2 can be found from the solution of this latter equation, that is, by Fourier's integral,

$$c_2 = (c_2)_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u u^2 du \right],$$

$$u = \frac{x}{2\sqrt{D_2 t}}.$$

The values of D_2 found when this assumption is made are fairly constant for different values of x, t and c_2 and average 1.47 and 1.32 for thallium sulphate and barium nitrate, respectively. The agreement between these values and those calculated from the Nernst formula (1.52 and 1.31) seems to indicate that the assumption inherent in the above formula is approximately true, that is, that the concentration of ions at any point is determined only by the number of ions that diffuse and that there is no formation of new ions from the undissociated molecules. This evidently requires that the mols of ions and of undissociated substance that diffuse through any cross-section be proportional to their respective concentrations, that is, that $dN_1/dN_2 = c_1/c_2$ and therefore, that $D_1 = D_2/n$, where n is the constant in the empirical concentration law $c_1 = Kc_2^n$. The relation $D_1 = D_2/n$ is not very far from true; which explains why the simple formula involving only the ionic concentration and diffusion-constant gives a close method of measuring the rate of diffusion of salts.

In this connection I wish to express my gratitude to Dr. A. A. Noyes at whose suggestion the work was undertaken and by whose constant interest and counsel it was enabled to be successfully carried on.

THE APPLICATION OF THE IONIZATION FROM HOT BODIES TO THERMOMETRIC WORK AT HIGH TEMPERATURES.

By O. W. Richardson.

THE fundamental relations between the ionization from hot bodies and their absolute temperature appear to be of so simple a character that the possibilities of this phenomenon for the investigation and determination of high temperatures ought not to be lightly disregarded. Two distinct general relations of this kind have now been discovered and have been verified for a number of substances with varying degrees of exactness. It is true that some of the experimental results deviate considerably from the theoretical requirements but these deviations are of such a character as to indicate that we have not yet discovered, or are unable to regulate, all the disturbing conditions, rather than to throw doubt on the general validity of the formulæ. If these effects are capable of furnishing valuable methods in high temperature thermometric work their further investigation and the investigation of such disturbing causes becomes a matter of great practical importance as well as of high theoretical interest.

The emission of ions by hot bodies may be regarded as analogous to the evaporation of a liquid or a votatile solid. This is particularly true of the negative ions, the supply of which appears to be practically inexhaustible. The number of positive ions that a body is capable of giving off diminishes progressively with the length of time that the body is heated. The emission of positive ions would thus appear to be more closely paralleled by the escape of the vapor of a volatile liquid from another less volatile which had dissolved a small amount of it. This is evidently a more complex case than the former and for that reason we shall practically confine ourselves in what follows to the phenomena exhibited by the negative ioniza-

tion, although it is to be borne in mind that many of the properties of the negative ionization are true, or something very similar is true, of the positive.

The first method which suggests itself as a possible way of applying this emission of ions to measure temperature has points of similarity with the application of the measurement of the vapor pressure of a liquid for the same purpose. On account of the small number of the ions per cubic centimeter which would be in equilibrium with a hot body, and for other reasons, we are unable to measure their vapor pressure directly; but we are able to measure a quantity which is nearly related to this, namely, the number of ions emitted by each square centimeter of the hot body per second. It is shown in works on the kinetic theory of gases that if p is the pressure of a gas or vapor the number n of molecules which leave unit area of any surface bounding it per second is $\sqrt{3/2\pi} \cdot p/mc$, where m is the mass and c is the square root of the mean square of the velocity of the molecules of the substance at the temperature in question. An exactly similar relation holds for the emitted ions and it has been shown by the author that the number of these emitted by unit area of surface of a hot body should be connected with the absolute temperature θ by the simple formula

$$n = A\theta^{\frac{1}{2}} e^{-b/\theta}.^{1} \qquad (1)$$

The quantities A and b are constants possessing a definite physical meaning; A is proportional to the concentration of the system inside the metal which emit the ions whilst b is a measure of the work done by an ion in getting free from the metal. The general applicability of this formula has now been abundantly verified[2] although there remains a noticeable lack of agreement as to the values of the constants A and b which have been obtained by different observers. This lack of agreement appears to originate in the following manner. The quantity b which measures the work required for an ion to escape from the metal seems to be very sensitive to the minute changes in the structure of the surface of the metal which either

[1] Camb. Phil. Proc., Vol. II., p. 286, 1901.

[2] O. W. Richardson, Phil. Trans., A, Vol. 201, p. 497, 1903 and A, Vol. 207, p. 1, 1906. H. A. Wilson, Phil. Trans., A, Vol. 202, p. 243, 1903. F. Deininger, Ann. der Phys., IV., Vol. 25, p. 285, 1908.

occur with continued heating, or arise from the expulsion of absorbed gas, or are due to the absorption of gas from outside the metal. The relative importance of these different factors and the best way in which the variability they introduce can be eliminated have not yet been fully worked out but it is satisfactory to note that the more recent investigations have shown a progressively increasing degree of consistency.

The method which is used to test the truth of formula (1) may be briefly indicated. If i is the saturation current per unit area of the hot metal at any temperature θ then, since n is the number of ions emitted by unit area of the surface per second, we have $i = ne$, where e is the charge on an ion. So that, introducing a new constant $A_1 = \log_e A/e$ we have

$$\log_e i - \tfrac{1}{2} \log_e \theta = A_1 - b \cdot \frac{1}{\theta}.$$

If we subtract one half of the logarithm of the absolute temperature from the logarithm of the current the resulting difference should be a linear function of $1/\theta$. The way in which this is the case is shown particularly well by the diagrams given by Deininger on pp. 304 and 305 of the paper cited above. These diagrams represent the emission of negative electricity from hot platinum, carbon and tantalum, and from these metals and also from nickel when coated with a thin layer of calcium oxide.

As an illustration of the way in which this method might be applied to the measurement of high temperatures we may take the problem of determining the electrical resistance of tantalum, between, say, 1500° C. and the melting point of this refractory substance, as a function of the temperature. It is quite an easy matter to determine simultaneously both the electrical resistance of a strip of hot metal and the saturation current per unit area. Full details of the method to be employed are given in the writer's papers.[1] Suppose that by means of thermocouples or some other standard method of high temperature thermometry we are able to determine the temperature of the tantalum up to 1500° C. The arrangements necessary for this purpose are described in Deininger's paper (*loc. cit.*). By making observations of the emission of ions and of the

[1] See especially Phil. Trans., A, Vol. 201, p. 497.

temperature we are enabled to construct the diagram giving the linear relation between $\log i - \frac{1}{2}\log\theta$ and $1/\theta$ for values of θ up to 1773° absolute. By extending this line beyond the limits of the observation we obtain $\log i$ in terms of θ at any temperature. We now discard the thermocouples: they are not much use at temperatures higher than 1500° C. under any circumstances: and observe only the values of i, the saturation current, and γ, the resistance of the wire. We thus obtain γ as a function of i, and i can be expressed in terms of θ by means of the diagram already constructed. In deducing the value the of θ from the value of i by means of the diagram it is convenient to proceed by a method of successive approximation. The diagram does not give θ in terms of i by inspection, since the ordinates are not $\log i$ but $\log i - \frac{1}{2}\log\theta$. The term $\frac{1}{2}\log\theta$, however, varies very slowly with θ when compared with $\log i$ so that we shall get very near to the correct value of θ if we take any reasonably near value of θ for this term. We may take for example $\theta = 1800°$ absolute. We therefore subtract $\frac{1}{2}\log_e 1800$ from the value of $\log_e i$ corresponding to the value of γ at the temperature which we wish to determine. Having found $\log_e i - \frac{1}{2}\log_e 1800$ we refer to the diagram and obtain the corresponding value of $1/\theta$. This value gives a value of θ say θ_1, which is very nearly identical with the correct value. We now calculate the value of $\log_e i - \frac{1}{2}\log_e\theta_1$, and referring to the diagram find a new value $1/\theta_2$. This process of successive approximation can be repeated indefinitely but it will be found in practice that the value θ_2 obtained at the second approximation in any ordinary case coincides with the true value θ_∞ within the limits of experimental error.

So far we have only indicated the way in which this method could be employed to obtain the absolute values of high temperatures and have considered neither its merits nor its demerits. Chief among its advantages must be reckoned its sound and direct theoretical foundation. The formula $i = A_1\theta^{\frac{1}{2}}e^{-b/\theta}$ has been deduced in a variety of ways more or less independent. But the claim of the formula as an expression of a general truth does not rest solely on the agreement of conclusions based on apparently different sets of assumptions. It is equally important to observe that it may be deduced from assumptions of a very general character.

In order to deduce the formula it is only necessary to assume (1) that the ionization is a function of the temperature, (2) that the emission of the ions is accompanied by a gain or loss of energy by the hot body, and (3) that the emitted ions behave dynamically like a gas when their concentration is so small that their mutual forces may be neglected. These assumptions are all so extremely probable that the result is practically placed outside the region of hypothesis.

It is to be borne in mind that there is nothing in the theory which demands that A_1 and b should not be functions of the temperature. On going into the matter more fully we should rather expect that they would depend on the temperature to some extent, possibly to a considerable extent. It is evident, however, from the experimental results, that the constants A_1 and b which enter into the formula for the saturation current are independent of temperature within the limits of accuracy of the investigations made up to the present. Since there is no theoretical warrant for this state of things the ultimate basis of the method must be regarded as empirical.

Another advantage of a more practical character arises from the extraordinary sensitiveness of the ionization from hot bodies to small changes of temperature. In the case of carbon for instance, the author found in a typical experiment that the saturation current at 1160° C. was 9×10^{-8} amperes, whilst at 1360° C. it had increased to 2.2×10^{-4} amperes. Thus in a range of only 200° C. the ionization changed in the ratio of about 2,500 to 1. This corresponds to an increase of about 10 per cent. of the value of the current for every degree rise of temperature. This great sensitiveness to change of temperature arises from the occurrence of the factor $e^{-b/\theta}$ in the formula; since, as is well known, this function changes very rapidly as the argument θ varies. For this reason the method would probably prove invaluable in any investigation the object of which was to test for the occurrence of small changes in the temperature of hot bodies due to any cause.

Of course, in making a series of observations over an extended range of temperatures the accuracy of the temperature determination is nothing like so great at present as what this degree of sen-

sitiveness would appear to imply, for the reason that the operations involved appear, in practice, to change uncontrollable conditions in a way which it is difficult to allow for. Since i varies very rapidly with θ it follows that θ varies very slowly compared with the change in i, so that an error of say 20 per cent. in the determination of the current would have no appreciable effect on the absolute temperature. In fact in the case of carbon already quoted it would have meant an error of less than 2° C. at say 1300° C. Considerable errors in the value of the current are therefore possible without seriously vitiating the temperature determinations.

The chief objection to this method of high temperature thermometry arises from the existence of these uncontrollable variations. However, they are already becoming less formidable as investigation progresses and the minutiæ of the phenomena are becoming better understood. It looks now as though this mode of procedure was within a measurable distance of becoming a satisfactory and practical instrument of high temperature research. Both this method and the next possesses additional advantages which it is unnecessary to enter into here, due to the fact that all the measurements involved are simple electrical measurements and that the apparatus required is such as can be found at hand or easily constructed in any physical laboratory.

The second method which is suggested depends on properties of the ionization from hot bodies which have been but recently discovered and the experimental knowledge which we are able to bring to bear on the question is even more meager than in the case of the first. To this extent the method outlined is more speculative than the first but this consideration is offset by compensating advantages.

Briefly stated the method consists in measuring the kinetic energy of the ions emitted by the hot metal; or, to be more exact, the value of $\frac{1}{2}mu^2$, where m is the mass of the ions and u their component of velocity perpendicular to the surface from which they are emitted. A way in which this may be done has been described by the author in collaboration with Mr. F. C. Brown.[1] The strongest point of this method is theoretical in character and rests on the fact

[1] O. W. Richardson and F. C. Brown.

that the quantity measured is independent of the properties of any particular substance. The quantities which enter into the theoretical formula are fundamental physical constants depending only on the dynamical properties of a perfect gas and on the laws of electrolysis. We are therefore independent of the particular properties of the substance with which we are working, so that the changes in the nature of the surface, which formed the most serious objection to the first method are, except under special circumstances, without effect on the second. If the theory is well founded we have in this case a direct appeal to the most fundamental measure of temperature, namely, the translational kinetic energy of the ions or of the molecules of a gas, to which they are equivalent so far as their thermal relations are concerned.

If we imagine a piece of metal, at a temperature sufficiently high for ions to be emitted, to be placed in an exhausted enclosure bounded by walls which are non-conductors of heat and of electricity, ions will be given off until a steady state is reached when as many ions return to the metal from the surrounding space in a given time as are emitted by the metal in the same interval. If the final equilibrium is to be thermal as well as electrical, in other words, if the second law of thermodynamics holds for this phenomenon, the energy carried away per second by the escaping electrons must be equal to that gained from those returning. In addition to this the components of the total momentum parallel to any three mutually perpendicular axes must remain unchanged. The only solution which appears to satisfy these conditions is that the distribution of velocity among the escaping particles must be identical with that among those returning. The latter can be calculated by the methods of the kinetic theory of gases. If n is the total number of ions emitted by any element ds of the surface perpendicular to the axis of x in unit time, then the number which have velocity components between u and $u + du$ is

$$n_u = n \cdot 2kmue^{-kmu^2}du.$$

The corresponding quantities for the y and z axes are

$$n_v = n\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmv^2}dv,$$

$$n_w = n\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmw^2} dw,$$

whilst the number which at the same time have velocity components between u and $u + du$, v and $v + dv$ and w and $w + dw$ is

$$n_{uvw} = n \cdot 2\frac{k^2m^2}{\pi} ue^{-km(u^2+v^2+w^2)} dudvdw.$$

In these formulæ m is the mass of an ion, and $3/4k$ is its average translational kinetic energy, k is inversely proportional to the absolute temperature, it is in fact equal to $\nu/2R\theta$ where R is the constant in the equation $pv = R\theta$ reckoned for one cubic centimeter of gas at 0° C. and 760 mm. pressure and ν is the number of molecules in one cubic centimeter of a gas under the same standard conditions.

The simplest way of applying this conclusion is to take two parallel plates whose dimensions are large compared with their distance apart. They can then be treated with sufficient approximation as infinite planes. A small hole in the lower plate admits a strip of hot metal which is flush with the upper surface of this plate, with which it is metallically connected, so that the lower plate and strip are always at the same potential. The lower plate and strip are always maintained at zero potential, being connected to earth, whilst the upper plate is insulated and connected to one pair of the quadrants of an electrometer and to a suitable additional capacity if required. Initially this plate also is at zero potential but subsequently charges up as the ions emitted by the metal strip reach it. This charging up produces a back electromotive force V tending to reduce the current i which therefore diminishes with lapse of time. It can be shown to follow from the theory already outlined that the relation between the current and the voltage is

$$\log \frac{i}{i_0} = -\frac{\nu e}{R\theta} V,$$

where i_0 is the initial value of the current when $V = 0$ and νe is the quantity of electricity required to deposit half a cubic centimeter of hydrogen by electrolysis.

Experiments by the author and Mr. Brown have shown that in the case of the ionization from hot platinum the required proportionality between $\log i$ and V is accurately verified provided θ remains constant and provided also that the hot metal has not been highly charged with electricity during its previous history. Charging the hot metal with electricity of either sign appears to produce peculiar changes in the energy of the emitted ions. This effect, which was discovered by Mr. Brown, is now being further investigated by him. He has found one result among others which is of special interest in this connection. That is that the peculiar state induced by the electric charge can be wiped out by heating the metal to a much higher temperature, so that after this treatment the theoretical formula is again obeyed.

The value of the constant $\nu\epsilon/R$ which when multiplied by $-V/\log_e i/i_0$ is equal to θ is theoretically calculable from the value of well known constants. So far the different determinations of this quantity have shown a considerable degree of variation, much more so than the probable errors of experiment would seem to warrant. The experimental values are distributed pretty evenly around the calculated value of $\nu\epsilon/R$ indicating that the theory is substantially correct. The deviations might be accounted for either as experimental errors or as arising from some disturbing cause affecting the phenomenon which has not yet been taken account of. The only experimental measurement which appears to have much chance of being seriously at fault is that of the temperature of the hot metal. This has been obtained by measuring its resistance. As the resistance of the metal is very low (it is a strip of foil whose dimensions are roughly $1 \times 3 \times .0005$ in millimeters) and as its temperature varies considerably from point to point of the strip there is bound to be some degree of uncertainty as to what should be taken to be the effective temperature of the hot metal. On the other hand one would expect a better agreement, than that which occurs, between the different values of $\nu\epsilon/R$ made with the same strip, since these only involve relative changes in the temperature. On the whole it looks at present as though there were some disturbing cause, perhaps related to the effect of an electric charge already alluded to, which has not yet been fully taken account of.

The great and obvious advantages of this method for standard thermometry at high temperatures lie in its theoretical directness and simplicity and the fact that it is a truly absolute method independent of the properties of any particular substance. All this of course rests on the assumption that the theoretical ideas underlying this development of the subject correctly represent the facts. The agreement between practice and theory which has so far been obtained makes the future of this phenomenon as an instrument of high temperature research look very promising. It seems quite clear that the further investigation of this subject is a matter of the very greatest importance from this very practical point of view.

It should be clearly understood that the primary object of both the methods which have been outlined would be to furnish a new standard of high temperature thermometry rather than to furnish an actual thermometer which could be used to determine temperature in practical cases. As a practical thermometer for high temperature work an instrument based on the resistance of some highly refractory metal or on optical methods would probably be much easier to construct and would work better. However, there seems to be comparatively little difficulty about the construction of a convenient practical instrument based on empirical principles. It is precisely when we consider our equipment of ultimate thermometric standards at very high temperatures that the deficiency of methods is most marked. When we arrive at the temperature at which, owing to the softening or incipient porosity of the materials which can be used for containing-vessels, the gas thermometer can no longer be employed, we have only one method left, that which is based on the emission of radiation from a perfectly black body. The theoretical basis of this has been criticized by recent writers so that it is of the utmost importance that some additional absolute standard should be found which can be used when the gas thermometer is no longer serviceable. The methods which are here outlined, based on the emission of electrons from hot bodies, show definite promise of being able to fill up this lacuna.

We have not specifically illustrated the way in which the second of the methods outlined above could be employed to measure some property of the body used in terms of the absolute temperature,

since the principles to be applied are precisely the same as in the first method. In each case to effect a comparison with some other absolute standard method such as the black body method it would probably be necessary to effect comparisons of both with some intermediate standard. This might be conveniently chosen as the resistance or specific resistance of the material employed in the electric emission method. In the case of the second method it might be easier to compare the optical emission rather than the resistance with the electric emission.

This paper perhaps requires some apology for the speculative attitude it takes up in regard to what is essentially a practical question. It is not professed that either of the methods which have been outlined could be applied at once with absolute confidence in the results. Despite much arduous work our knowledge of the emission of ions from hot bodies is still very incomplete. Much more work will have to be done before we can rely with certainty on theoretical conclusions from experiments of this character. It is particularly essential that experiments similar to those already made should be carried out with other materials and with the same materials under intelligently varied conditions. It is only by an exhaustive study of this kind that we are likely to discover the best material for the standard substance and the detail of the method according to which the experimental measurements should be carried out in order to achieve success in thermometry. It is possible that further inquiry would show that the phenomena of electric emission are not capable of being reduced to the degree of precision demanded by the work of this nature. This is extremely unlikely — the conclusion is almost denied even by the present approximate state of the subject — but even if it turned out to be the case the work that had been done would not be wasted. The data that would be obtained are of very great theoretical interest, and on this account alone would well repay the labor involved. When the thermometric possibilities are added to this the field looks a very promising one.

The importance of the question of which it offers the possibility of a solution would appear to sufficiently justify the occurrence of this short paper. If it succeeds in stimulating others to a practical

interest in the subject from this point of view it will have completely achieved its purpose.

APPENDIX.

An idea of the reliability of the results which ought to be obtainable by applying the first method with reasonable care at the present time can be obtained from the diagrams on page 304 of Deininger's paper (*loc. cit.*). If the lines were extended so as to obtain temperatures outside the explored region in the manner indicated above there is no reason why the errors of experiment should be greater than those within the known region. The deviation of the experimental points from the straight line will thus show what kind of errors we shall have to expect in using this method to determine temperatures. If we take the points which fall *furthest* from the straight line we shall obtain a measure of the greatest error that we are likely to encounter. By taking a series of measurements the error will be averaged out and the probable error will be very much less than this. The points which fall furthest from the straight lines in these diagrams correspond to the following deviations from the temperature as given by the straight lines.

Conductor.	Approximate Absolute Temperature.	Maximum Error, Degrees Centigrade.
Platinum	1639° abs.	8° C.
Tantalum	1639	11
Carbon	1429	5
"	1663	4

Two numbers have been given in the case of carbon, as the first one, that which gave the maximum error of 5°, was the first observation taken and corresponded to the lowest temperature on the table. For these reasons there might be expected to be something exceptional about it. The other points all lie much closer to the curve, so the next furthest away has been taken as being more representative.

It is to be borne in mind that the numbers in the preceding table represent the maximum deviation out of a large number of observations. The curve for carbon covers 24 observations, that for tan-

talum 35, and that for platinum 22. In any actual experiment in which this method was used to determine temperatures it would naturally be arranged that a large number of observations would be taken so that the expected error ought to be much less than these values. As they stand, however, the errors are probably at least as small as could be obtained by any other thermometric method at these temperatures.

PRINCETON, N. J.,
April 22, 1908.

DIFFERENTIAL ELECTRIC DOUBLE REFRACTION IN CARBON BISULPHIDE.[1]

BY C. F. HAGENOW.

THE phenomenon of double refraction in dielectrics when subjected to an electric strain was discovered by Kerr[2] and later studied by a number of other investigators.

The methods employed were, generally, to place the dielectric between parallel electrodes, maintained at a known difference of potential, and this system between crossed or parallel nicols (set at 45° to the field) in line with a source of light. The resulting double refraction was measured by a Babinet compensator. The potential was supplied by a static machine, induction coil or storage battery.

The law obtained from these investigations is expressed by the formula

$$\delta = \pm \frac{P^2 B l}{a^2} \tag{1}$$

where δ is the phase difference in wave-lengths between the two emerging components of light (vibrating, of course, at right angles to each other); P the potential in electrostatic units; l the length of the electrodes and a their distance apart in centimeters; B the electro-optical constant for the particular dielectric considered.

In determining B several difficulties are met with. An error of one per cent. in the value of a (and this must of necessity be taken small) causes an error of two per cent. in the result. For the same reason the error in potential, a factor necessarily large and hence difficult to measure, produces a double error in the result. The presence of small particles in the liquid often adds to the inaccuracy

[1] Read at the Chicago meeting of Section B of the American Association for the Advancement of Science, January, 1908.

[2] J. G. Kerr, Phil. Mag., 50, pp. 337 and 446, 1875; 8, pp. 85 and 229, 1879; 9, p. 157, 1880; 13, pp. 153 and 248, 1882; 20, p. 363, 1885; 37, p. 380, 1894; 38, p. 144, 1894. Rep. British Association for the Advancement of Science, p. 157, 1892.

of the compensator settings by causing disturbances in the field of view.

The condition of the CS_2 also affects the value of this constant, though to just what extent is not definitely known. Quincke[1] found considerable variation in seemingly pure CS_2 and obtained values of B differing as much as 20 per cent. He shows a comparison of results obtained from two lots of the liquid; the one specially prepared for him by Kahlbaum and the other purified by himself by shaking with dried $CuSO_4$, distilling and filtering. On comparing the results obtained from these two, other parts of the apparatus being the same, the variation is not greater than 4 per cent. from the mean. He found further, on introducing a Leyden jar to steady the potential, a considerable increase in the observed effect. His results also indicate a decrease in the value of B with the length of the electrodes.

Quincke claimed an accuracy of 1/150 mm. in measuring a, and .000062 λ in the compensator, though he could hardly have obtained settings to that degree of accuracy in the presence of the fluctuations caused by the static machine. He ascribed the lower value of B, obtained without the use of the Leyden jar, to the rapid changes in potential. He used a long range Kelvin electrometer and also a Righi reflection electrometer to measure the potential and a Babinet compensator to measure the phase difference.

Later Schmidt,[2] using CS_2 as a standard of comparison, found that the presence of foreign substances did not appear to affect it to the extent of Quincke's results. He attributed the error chiefly to the measurement of the distance between the electrodes and the uncertainty of the setting of the compensator on account of the particles in the field of view. He gives no details as to purification.

Lemoine[3] made a determination of B, laying claim to greater accuracy than Kerr and Quincke, but he states nothing as to his method of purifying the liquid. He employed an absolute electrometer and a Babinet compensator. A correction was also made for the length of the electrodes, on account of the error due to the

[1] G. Quincke, Wied. Ann., 19, p. 729, 1883.
[2] W. Schmidt, Ann. d. Physik, 7, p. 142, 1902.
[3] J. Lemoine, Compt. Rend., 122, p. 835, 1896.

edges of the latter, which is about one per cent. He gives $B = 3.70 \times 10^{-7}$ (using white light and a red glass as a filter) as the average of 21 series of observations, which did not depart from the law as stated above by more than one per cent.

The most elaborate attempt at the purification of CS_2 has very recently been made by Blackwell [1] in his investigation of its electric dispersion. However, he does not seem to think this treatment absolutely essential to the experiment. His work concerns itself chiefly with the relative values in the spectrum. Great care was taken in the preparation of the electrodes. A storage battery was employed, and the potential kept practically constant during the experiment. The dispersion was obtained by photographing the spectrum crossed by the dark band — using a spectroscope and Babinet compensator — and then measuring with a telescope the relative shift of the band on the negative.

The average measurements of the observed shifts of the band in different experiments under practically uniform conditions vary as much as five per cent. from the mean, which is greatly in excess of the refinements employed in the construction of the apparatus. However, his object was to obtain relative retardations, and these were found in the case of each experiment separately, using the retardation of sodium light as a standard of comparison. The results so found agree much more closely, the error not exceeding two per cent. He obtained an absolute value of the retardation for sodium light of 7.04×10^{-7} cm. at 24° C. and 56,000 volts per cm. This corresponds to $B = 3.57 \times 10^{-7}$, subject, of course, to the variation noted above.

The main object of the present investigation undertaken at the suggestion of the late Dr. Brace was to determine B for various colors, using a highly sensitive method of measuring the phase difference, viz., the Brace, half shade elliptic polarizing system.[2] The fact that it permits the use of very low potential has already been taken advantage of by Elmén.[3]

In the present case its high sensibility is used advantageously in

[1] H. L. Blackwell, Proc. American Academy of Arts and Sciences, Vol. 41, p. 645, 1906.

[2] D. B. Brace, PHYS. REV., 18, p. 70; 19, p. 218, 1904.

[3] G. Elmén, PHYS. REV., 20, p. 54, 1905.

determining a change of a complete wave-length. The compensator is first set for a match, with no electric field, then the potential applied and increased until a match is again obtained. This method avoids the necessity of taking into account the variation in the double refraction of the mica strips, for different colors, and also of calibrating the compensator.

The potential was supplied by a static machine and measured by a Kaufmann[1] form of absolute electrometer constructed for the purpose. As this was probably the least accurate part of the apparatus, the care taken in its adjustment and use may well be given a more detailed description.

The movable disk was suspended by a bifilar of phosphor bronze wire, adjustable in length, spread and torsion. On the axis of the disk was mounted a small plane mirror and the deflections observed by the telescope and scale at about a meter distance.

The fixed plate and guard ring were first carefully leveled. Then three glass blocks of 3.115 mm. thickness (accurate to .005 mm.) were placed on the fixed plate, which was raised parallel to itself on its insulating screw until the blocks touched the movable disk. Any tipping of the latter due to this contact was detected by a microscope cathetometer for one direction, and by a telescope and scale for motion at right angles to it. The distance between the fixed and movable plates was also measured by the microscope cathetometer; this being simply the thickness of the glass blocks plus the distance through which the fixed plate was raised, beginning at any desired point, until the instant of contact of the blocks with the movable disk. Of course this distance was made to conform with that between the guard ring and the fixed plate.

The wires of the bifilar were then twisted until the disk was rotated through nearly 90 degrees, the position of greatest sensibility, and the system calibrated by the use of a series of nine weights (accurate to .0001 gram) suspended from a hook centered in the framework above the disk. After standing in adjustment about a week, the instrument gave a very constant calibration. However, calibrations were always made just before and after a set of observations. A number of readings were also compared with results

[1] Cf. J. E. Almy, Ann. d. Phys. (4), Vol. 1, p. 508, 1900.

obtained from spark potentials and were found to check within an average of less than one per cent.

The static machine was driven at a constant speed and the potential changed by shunting with a variable point discharge.

The disposition of the optical apparatus is shown in Fig. 1. Light from the sun was focused on the slit m_1 by the lens L_1. The second slit m_2 is conjugate to m_1 through the lenses L_2 and L_3 and the dispersing prism A. The angular position of the latter was

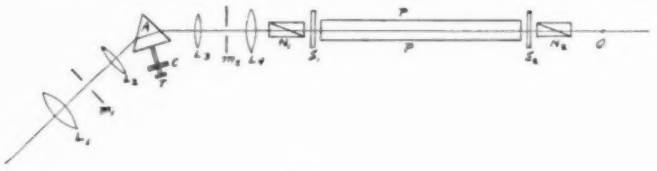

Fig. 1.

controlled by a screw T and its positions calibrated for definite wave-lengths passing through m_2 by use of the scale C. The lens L_4 focused the beam on the eye placed at O. The nicol N_1 polarized the light at 45 degrees to the lines of force and N_2 was set for extinction. The half shade S_1 was placed so that its principal axis was at 45 degrees to the plane of vibration of the polarized light (giving maximum illumination) with its edge perpendicular to the condenser plates; so that any variation of color might be the same on both sides of the dividing line. P is the tube with the electrodes and S_2 the compensator. A telescope was usually mounted at O to magnify the field of view.

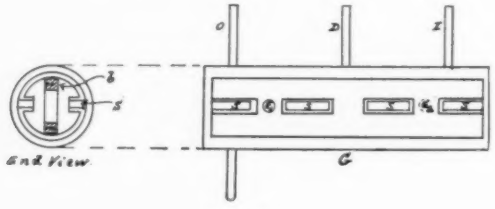

Fig 2

The electrodes were of nickeled brass 50 cm. long and about 9 mm. wide. Fig. 2 illustrates the arrangement, as designed by Mr. L. B. Morse who used them previously. The plates were kept at

the proper distance apart by eight glass blocks *b* (see end view, Fig. 2) about 13 mm. long, a little more than 2 mm. wide and 1.97 mm. thick, the last dimension representing the distance between the electrodes.

To hold them in place, four of them were drilled with holes a little less than 1 mm. deep to fit corresponding pegs in the electrode. The pressure of eight springs *S* against the walls of the enclosing tube held them firmly together, and rendered them also fairly secure against displacement in the tube.

The tube *G* had five openings; the inlet tube *I*, outlet *O*, E_1 and E_2 for the insertion of wires connecting to the static machine, and the tube *D* to facilitate removing air bubbles which were caught between the glass blocks. Platinum wires sealed in short glass tubes which just fitted into E_1 and E_2 made electrical connection with the electrodes. These were cemented in place after contact with the electrodes was assured. The tube was sealed at the ends by thin cover glasses, cemented on by a paste, which, while resisting the action of the CS_2, had the further advantage of not drying to perfect hardness and thus causing strain and consequent double refraction. However, the cover glasses were tested for double refraction and many had to be rejected on account of showing evidence of strain.

The whole was mounted on a base together with two large bottles serving as reservoirs for the liquid; one connected to the tube *I*, the other to *O*. The first of these bottles was provided with a filter cup sealed into the neck by plaster of Paris; the other one, joined to the tube *O*, was closed with a rubber stopper. This gave a continuous flow from the filter cup through the main tube and into the second bottle, from which the liquid was drawn for fresh distillation.

Stopcocks provided for the different requirements of the system which was intended to keep the liquid, when once clean, from contact with the air, and at the same time to allow of introducing fresh liquid when desired. The liquid was filtered and forced through the system by means of compressed air.

No attempt was made towards complete purification, but care was taken to have the liquid free from water and dust particles,

which in the reports of previous investigators, as well as from the writer's own experience, seem to be the only essential disturbing factors. Moisture especially caused the greatest trouble and delay.

The CS_2 was first distilled with fresh lard and fused $CaCl_2$, usually about three times; though considerable variation in their treatment seemed to cause no great change in the results. Attention will be called to this fact again later. A 32-candle-power incandescent lamp in an asbestos oven served admirably as a safe heating arrangement. After distillation the liquid was filtered through the porous cup into the receiving bottle above mentioned; and, after some of the liquid had been run through the system, the tube was filled and all the air bubbles removed by manipulating the flow of the liquid and by tipping the tube. In this way any particles present to begin with are gradually carried out into the second bottle to be filtered out.

TABLE I.

Temperature 25° *C.*

$\lambda\mu\mu$	Scale.	Average.	Potential.	$B \times 10^7$
	539			
	538			
430	538	538	40.75	4.67
	518			
450	514	516	42.30	4.34
	466			
500	465	465	46.00	3.67
	417			
550	418	417	49.35	3.19
	379			
590	380	379	52.05	2.87
	365			
600	367	366	53.00	2.76
	334			
650	333	333	55.30	2.54
700	310 (?)	310 (?)	56.90	2.40 (?)
430	290			
(2δ)	292	291	58.20	4.58
450	257			
(2δ)	258	257	60.45	4.25

Observations were taken as follows: The tube being filled and in place, the compensator was set for a match on any color.[1] The potential was then applied and gradually increased until a match was again obtained. A second observer read the corresponding deflection of the electrometer. Readings were taken at different points throughout the spectrum. B was then calculated according to formula (1). Table I. shows one set of readings in detail. The CS_2 used was distilled three times; twice with $CaCl_2$ and lard, the third time with $CaCl_2$ only. In case of the shorter wave-lengths it was possible to produce a change of two wave-lengths, as shown in the last two readings in the table.

Table II. gives another set of readings taken about a month later with CS_2 only once distilled with fused $CaCl_2$. The calibration of the electrometer was different but the values of B are only slightly lower.

TABLE II.

Temperature 25° *C.*

λ	Scale.	Av.	Potential.	$B \times 10^7$	λ	Scale.	Av.	Potential.	$B \times 10^7$
	477					265			
	478					264			
	477					265			
430	476	477	41.55	4.50		263			
	450					265			
						265			
450	452	451	43.40	4.12	650	267	265	55.90	2.48
	401								(?)
500	400	400	46.80	3.54	700	221	221	58.70	2.25
	349				430	218			
	351				(2δ)	217	217	58.90	4.48
550	349	350	50.20	3.08		178			
	313					178			
	312				450	177			
	314				(2δ)	178	178	61.4	4.12
	311					88			
590	312	312	52.75	2.79	500	88			
	304				(2δ)	87	88	66.85	3.47
	299								
	304								
	302								
	299								
600	299	301	53.50	2.71					

[1] It was then matched for all colors.

TABLE III.

Summary.

No. of Ex.	1	2	3	4	5	B Av.	$B \times \lambda$	Per Cent.
λ 430	—	4.67	4.50	4.47	4.51	4.54	1952	116.2
λ 450	4.32	4.34	4.12	4.10	4.11	4.20	1890	112.5
λ 500	3.67	3.67	3.54	3.55	3.54	3.59	1795	106.8
λ 550	3.19	3.19	3.08	3.07	3.07	3.12	1716	102.1
λ 590	2.94	2.87	2.79	2.84	2.79	2.85	1681	100.0
λ 600	2.80	2.76	2.71	2.69	2.70	2.73	1638	97.5
λ 650	2.57	2.54	2.48	2.50	2.45	2.51	1632	97.1
λ 700	—	2.40	2.25	—	2.31	2.32	1624	(?) 96.7

Table III. is a summary of five different sets. The values of B are slightly lower in the last three than in the first two. This difference is hardly to be accounted for by the change in the condition of the liquid used in beginning the last set. For in experiment 4 some of the liquid first used was again employed after being redistilled and filtered. In fact, owing to the impossibility of entirely emptying the system of one lot of the liquid before refilling it, the portion experimented upon at any given time was always more or less of a mixture. The average values of B are plotted in Fig. 3.

The actual retardation is given by $\delta \times \lambda$, that is, by

$$\lambda \times \frac{P^2 B l}{a^2}$$

from formula (1). For purposes of comparison it is sufficient to find the product $B \times \lambda$ at the different points of the spectrum. These values are shown in Table III. and are plotted in Fig. 4. For com-

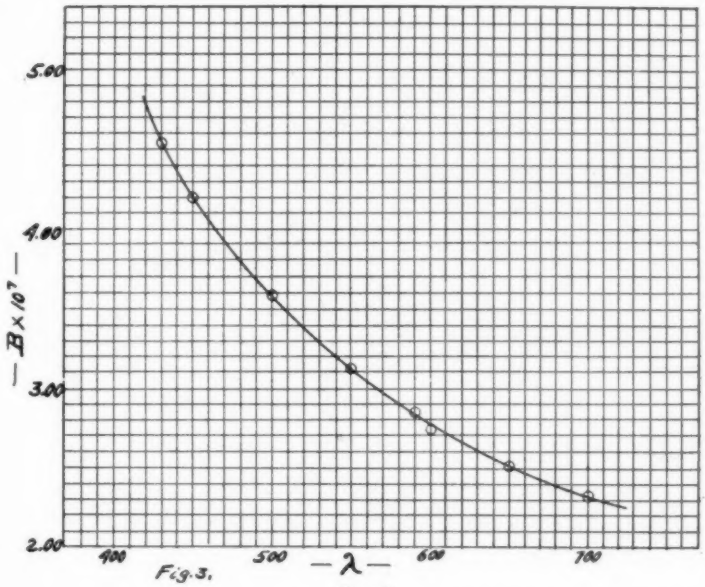
5.00
4.00
3.00
2.00
— B × 10⁷ —
400
500
600
700
— λ —
Fig. 3.

Fig. 3.

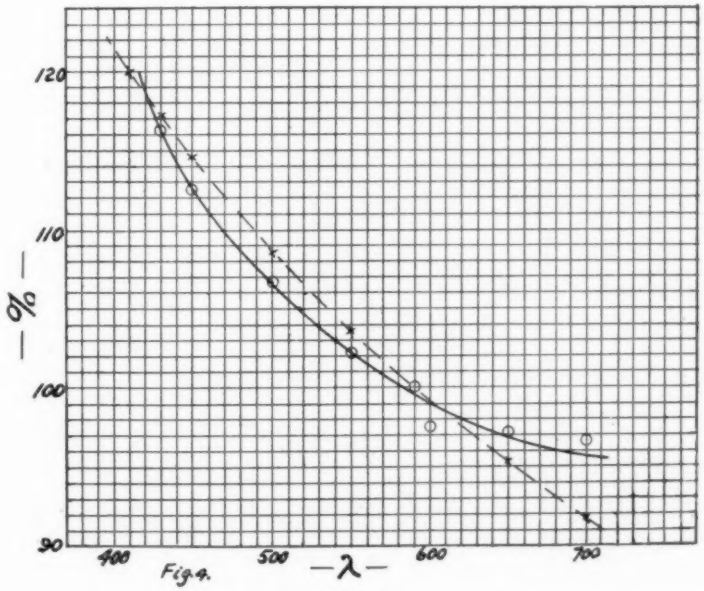
120
110
100
90
— % —
400
500
600
700
— λ —
Fig. 4.

Fig. 4.

parison, the curve, according to Kerr[1] is added, shown in dotted lines. This is plotted according to his statement that the retardation varies inversely as the square root of the wave-length. The departure of the results of the present investigation from this law is apparent from the figure. The writer's curve agrees closely with a similar curve of Blackwell[2] in this respect.

The abrupt change in the values of $B \times \lambda$ about 600 $\mu\mu$ seems difficult to account for. Anything that might have caused a constant error in this region of the spectrum was carefully examined, but no inaccuracy was discovered.

As to the accuracy of the various measurements and constants involved in the experiment, it is believed that they are well within the limits set by the conditions of the problem itself. The positions of the dispersing prism were calibrated by means of the Fraunhofer lines, and the calibration was checked up after the experiment. The micrometer screw controlling the prism could be set to a half of one $\mu\mu$.

The glass blocks separating the electrodes might be uncertain as to thickness as much as .01 mm. which would affect the result not more than one per cent. The setting of the compensator for the match, before the potential was applied, was easily accurate to less than 0.2 per cent. and the settings for the various potentials used may be seen from Tables I. and II. which are typical. Thus the total range of the scale was 900 mm., and it was possible to determine a match to one division of the scale in the best instances, and within three divisions of the mean in the worst cases. This means an accuracy of 0.2 per cent. in the shorter wave-lengths and not more than 0.5 per cent. in the larger ones. The settings for wave-lengths greater than 650 $\mu\mu$ were found to be too uncertain to be of any value.

At every match the color of the field would change to the complimentary tint, which proved to be as delicate a test of uniformity as the match of intensity itself and in the blue end of the spectrum was the only means of determining the match.

[1] J. G. Kerr, Rep. British Association for the Advancement of Science, p. 157, 1892.

[2] H. L. Blackwell, Proc. American Academy of Arts and Sciences, Vol. 41, p. 650, 1906.

The two wave-length retardations as shown in Table II. are interesting as showing the uniformity of the formula for greater retardations. These values have not been used in the averages.

Experience showed that a much greater dispersion might have been used with sunlight to advantage. A more nearly monochromatic light would undoubtedly make closer settings possible in the red end of the spectrum.

These experiments were all performed at a nearly constant temperature of 25° C. It was noticed that the presence of particles caused a considerable increase of the potential necessary to get the same double refraction, which can be explained by the greater conductivity of the liquid. On allowing a fresh supply to flow into the tube from the receiving bottle the liquid would at once regain its former state. According to Quincke,[1] particles have the same effect as decreasing the distance between the electrodes, *i. e.*, increasing the double refraction. But this effect is evidently more than offset by the charge carrying capacity of the particles.

When sparks passed through the liquid the effect was the same as that caused by particles (particles of carbon probably being produced), and a new supply had to be admitted.

The writer performed a series of similar experiments a year before the present set. The same apparatus was employed with the exception of the electrometer, instead of which a spark gap was used. The results were not deemed sufficiently reliable for the purpose of the investigation, though the greatest variation in the value of B was 5 per cent. ; and, comparing averages with the present set, the differences are not greater than 3 per cent. The method of purification was the same, though various combinations of liquids were used on account of the circulating system used in connection with the tube.

In conclusion it would seem that a fairly stable condition of CS_2 for optical purposes can be obtained by a simple process of distillation and thorough filtering, and that this treatment allows of considerable variation without corresponding changes in the results.

It is not possible at this stage to make a systematic comparison of the values of B with those obtained by others ; since, owing to the difference in method or object in view in previous investigations,

[1] G. Quincke, Wied. Ann., 19, p. 758, 1883.

the data do not correspond. Quincke, in the reference given above, gives values ranging from 2.877 to 3.544 for sodium light. In the particular case where he used electrodes 47 cm. long his values vary from 2.877 to 2.981. Lemoine does not state the exact wave-length of light used, and Blackwell gives only one instance of the absolute value of the constant for sodium light; but, as noted above, this varies considerably in the different experiments.

As to the dispersion, the results do not bear out the law stated by Kerr, but give a curve steeper at the blue end of the spectrum and flatter at the red end, agreeing with the results obtained by Blackwell.

Finally the writer wishes to thank Dr. Skinner and Dr. Almy for their kind assistance and many helpful suggestions.

BRACE LABORATORY OF PHYSICS,
UNIVERSITY OF NEBRASKA, LINCOLN.

SOME STUDIES IN SHORT DURATION PHOSPHORESCENCE.

By Chan. W. Waggoner.

THE experiments which follow deal with the decay of phosphorescence in certain compounds after excitation by the ultraviolet light from the iron spark. Messrs. Nichols and Merritt[1] have studied the decay of phosphorescence in sidot blend and other long-time phosphorescent compounds throughout a certain range. They find that the decay curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas is a straight line for small values of t, and that it changes to a curve concave toward the axis of t as t increases; but for still larger values of t, the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words, the decay curve consists of two straight portions which gradually merge into each other.

Werner,[2] using a photographic method, and working with a long-time Sr—Zn—CaF_2 phosphorescent compound, found when the results were plotted with $I^{-\frac{1}{2}}$ as ordinates and corresponding times as abscissas the same kind of curves as were obtained by Nichols and Merritt. In the method used by the latter experimenters it was not possible to obtain points on the decay curve closer than four tenths of a second after the exciting light was shut off; and the first point in the curve given by Werner is twenty-one seconds after shutting off the exciting light. The study of the decay curve immediately after excitation has ceased was suggested to the writer by Professor Merritt, who had designed a phosphoroscope for this work. It was found, however, that even when operating the phosphoroscope at its slowest speed, the decay of sidot blend was too slow to be measured with accuracy and ease.

[1] Phys. Rev., Vol. 21, p. 247, 1905; Vol. 22, p. 279, 1906.
[2] Ann. der Phys., Vol. 24, p. 164, 1907.

Only by the use of infra-red rays was it possible to increase the decay sufficiently to determine the shape of the curve for the initial decay.

The limits of the operations of the phosphoroscope being fixed, it was found necessary to prepare phosphorescent compounds whose decay was very rapid and still of sufficient intensity to measure. A number of these compounds were prepared and studied along with several specimens of willemite whose decay was suitable.

METHODS OF PREPARING THE PHOSPHORESCENT COMPOUNDS.

In preparing the compounds, the methods given by Wiedemann and Schmidt[1] and Andrews[2] were followed. The ease with which these compounds may be prepared, and the intensity of the phosphorescent light given off when they are excited by the spark, seems to warrant a rather detailed account of their preparation.

A salt of manganese, in this case $MnSO_4$, was used as the active agent. Lenard and Klatt[3] found that the intensity of the compound is less affected by varying percentages of manganese, than with any of the other active agents. The compound consists of an inactive salt, an active salt, such as manganese, and a flux.

$ZnCl_2 + MnSO_4$. — Some zinc chloride prepared from metallic zinc was dissolved in a small quantity of distilled water. A small trace (usually less than one per cent.) of $MnSO_4$, dissolved in water, was added to the $ZnCl_2$ solution and the whole brought to the boiling point. An equal volume of sodium silicate, as the flux, was then added and the whole evaporated to dryness. On being exposed to the spark, faint green phosphorescence could be seen. It was then placed in a porcelain crucible and heated to a bright red for two hours. When cool it showed pale green fluorescence when exposed to the spark and when the exciting source was cut off, it was found to have considerable bright green phosphorescence. A sample of the powder at this point was kept and marked $ZnCl_2$ no. 1. The remainder of the powder was heated to a bright red for three hours and when cool showed both fluorescence and phosphorescence of greater intensity than did $ZnCl_2$ no. 1. A sample of

[1] Wied. Ann., Vol. 54 p. 604, 1895.
[2] Science, Vol. XIX., March, 1904.
[3] Ann. der Phys., Vol. 15, p. 243, 1904.

this was saved and marked no. 2. The remaining powder was heated two hours at a bright red and on examination when cool, it was found to have lost some of its original phosphorescent intensity. This was marked $ZnCl_2$ no. 3.

$CdCl + \times MnSO_4$. — Substituting CdCl for $ZnCl_2$ but giving it exactly the same treatment it was found that it was necessary to heat the compound at a bright red for three hours before the phosphorescence color was very intense, and that subsequent heating had no marked effect on its phosphorescence intensity when exposed to the spark. The fluorescence color was pink, and the phosphorescence dark red.

$CdSO_4 + \times MnSO_4$. — Some $CdSO_4$ was dissolved in water with a small trace of $MnSO_4$ and the whole heated to dryness without adding the flux. The resulting white powder showed pale yellow fluorescence and an orange-yellow phosphorescence of much longer duration than the zinc compounds.

$ZnSO_4 + \times MnSO_4$. — $ZnSO_4$ substituted for $CdSO_4$ and treated in the same way resulted in a white powder which showed pink fluorescence and bright red phosphorescence, but the intensity was too small to be measured by the method used.

Some "chemically pure" calcium sulphide was purchased with the view of trying to prepare compounds of CaS and $MnSO_4$, but it was found to be already an active phosphorescent compound having a brownish-red color.

Two large pieces of willemite, showing brilliant green phosphorescence with the iron spark were studied. It was found that their rates of decay were not the same. The sample having the slowest decay was marked willemite no. 5. The sample having the very rapid decay was crushed into a fine powder, a sample made into a screen and marked willemite no. 1. A part of the powder was heated to a bright red heat in a porcelain crucible for forty-five minutes. This was marked willemite no. 2. The remainder of the powder was heated for two hours at a bright red, and marked willemite no. 3.

One $ZnCl + \times MnSO_4$ sample made by W. S. Andrews, Schenectady, N. Y., was also studied.

For purposes of study, screens were made by placing the phos-

phorescent powder on small squares of heavy dark brown cardboard, the cards having been covered first with white "Zapon" varnish.

METHODS OF MEASUREMENT.

The phosphoroscope used in these measurements is shown in Fig. 1. It consists of a disc D, fastened to a cylinder L, rotating

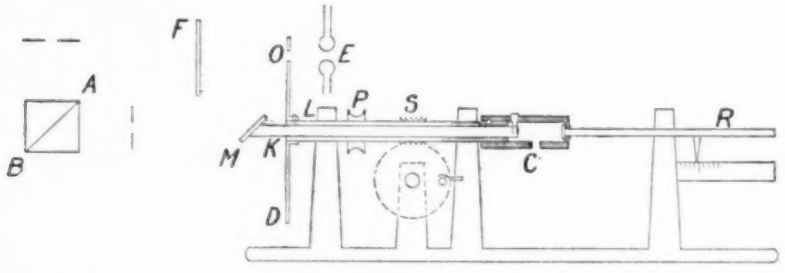

Fig. 1.

about a horizontal axis. On the inside of L is a shaft K which rotates at the same speed as the cylinder. On the end of K is a plane mirror, placed 45° to the axis of the shaft, and by use of the mechanism at C the position of the mirror, relative to any point on the disc D may be shifted while the disc is rotating. The disc has an opening at O, through which the light from the spark E, may pass each successive revolution, and excite the specimen placed at F. Now if the mirror is in the position shown it will reflect into the slit of a spectrophotometer the light which comes from the phosphorescent screen F, while it is being excited by the spark. By moving the rod R, the mirror is turned so as to reflect the light from the screen F into the spectrophotometer some time after excitation, and in this way the intensity of the phosphorescence after successive excitations may be measured by the spectrophotometer AB. The cylinder L is driven by a motor belted to it over the pulley P. S is a worm driving a cog wheel, which serves as a device for recording the speed by making an electric connection with a chronograph once in every hundred revolutions of the disc. Current operating the motor was taken from a direct-current source having a special device for maintaining constant voltage, and the speed of the motor was found to remain almost constant. The

disc D has a second half-disc fastened to the first (not shown in the figure) by which it was possible to change the size of the opening at O. The essential advantage of this phosphoroscope over others is that the decay of the phosphorescent light may be studied without changing the time of excitation. Another feature of this method is that settings on the spectrophotometer for any curve may be repeated as often as desired and the time taken for the determination of each setting may be as long as desired. The results shown in the curves that follow were determined from two different settings of the spectrophotometer for each point, and the plotted point represents the average.

The source of excitation was the spark between iron terminals. An induction coil was connected to a source of alternating current of 60 cycles frequency; a small condenser being connected in multiple with the spark gap. In order to study the effect of decreased time of excitation, it was found necessary to increase the frequency of the spark, this being accomplished by connecting it to a source of alternating current giving 140 cycles. With this higher frequency the chances of the spark exciting the screen at each turn of the disc is greater; also the higher frequency could be used as a check on the curves taken at the lower frequency.

An incandescent lamp connected to a constant potential source was used as a comparison source in the spectrophotometric measurements.

Discussion of Results.

The curves shown in Fig. 2 are decay curves typical of three substances studied. They are plotted with $I^{-\frac{1}{4}}$ as ordinates and corresponding times as abscissas. It will be seen that the curves have the same general characteristics as those for long-time phosphorescent substances, *i. e.*, the curve consists of two straight lines merging into one another. Curve A shows a very rapid decay, and it is quite difficult on account of the small intensity of the light to follow the second straight portion of the curve very far.

It will be seen that in each curve one point has been plotted to the left of the zero on the ordinates. This observation is made on the fluorescent light, *i. e.*, it is the intensity of the light coming from the screen when the mirror is in position to reflect the light which

comes from the screen during excitation. The zero point, or the point where the exciting light fails to be reflected into the spectrophotometer, was determined by placing a piece of white paper in place of the screen.

On examination of the time of excitation it will be found that there can be at most only 120 sparks per second and during the time of excitation given in the curves in Fig. 2 it will be seen that three sparks per revolution of the disc is the maximum number that could pass while the screen is being excited. In fact it is highly improbable that this number really do pass during excitation, and it

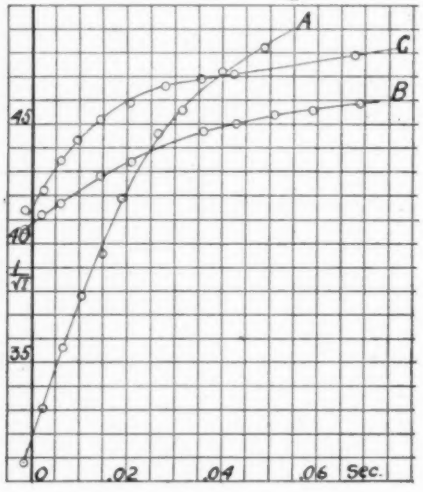

Fig. 2.

Decay curves.

Curve *A*. Willemite No. 5, time of excitation .026 sec.
" *B*. Andrews $ZnCl_2$, " " " .027 "
" *C*. $ZnCl_2$ No. 3, " " " .026 "

would seem then that the excitation may vary. However, it will be remembered that these excitations follow each other very rapidly; for example, in curve *B*, Fig. 2, the rotating disc makes a complete revolution in .108 sec., and as something like 10 to 20 seconds were taken to make the setting of the spectrophotometer, whatever changes take place in the spark during successive excitation, the reading is an average value of the intensity at that point. In

order to make sure of this, readings were taken starting with the lowest intensity and ending with the highest: then starting with the highest and following the decay to the lowest value of intensity, the points plotted being an average of the two settings for each point on the curve.

A question might also arise, as to how the decay curve for a substance would vary if the points on the curve were determined by observing the decay after a single excitation, instead of by noting the time for the intensity to fall to a fixed value and then re-exciting to determine the next point, and so on. Messrs. Nichols and Merritt[1] have shown that the curves taken on sidot blend with the spectrophotometer for the first seven seconds of the decay are straight lines when plotted with $I^{-\frac{1}{2}}$ as ordinates and corresponding times as abscissas. These curves were taken by noting the

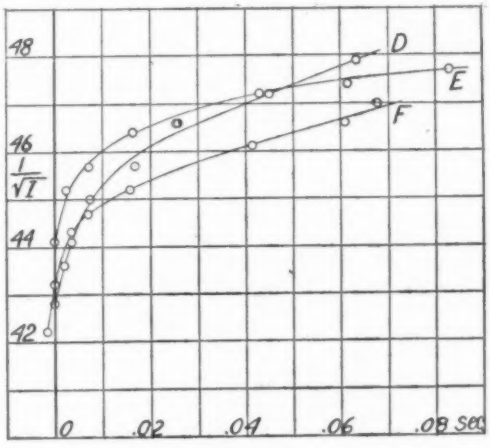

Fig. 3.

Showing the decay in different substances.
Curve *D*. CaS, time of excitation .033 sec.
" *E*. $CdSO_4$, " " " .032 "
" *F*. $CdCl_2$, " " " .031 "

time required for the intensity to fall to a fixed value, then re-exciting and noting the time to fall to a different intensity. Comparing the curves taken in this way, with the curves they give for the decay of the total intensity, by noting the intensity at different

[1] PHYS. REV., Vol. XXI., p. 247, 1905, and Vol. XXIII., p. 37, 1906.

times after one excitation, it can be seen that the curves are similar in shape so far as those taken with the spectrophotometer have been carried.

It will be noted that in practically all the substances studied, the measurable portion of the decay is over in .07 second. Some of the substances may, however, be seen in a dark room for a very much longer time.

The curves shown in Fig. 3 indicate a much slower decay than those shown in Fig. 2. The initial decay, however, is quite rapid. These

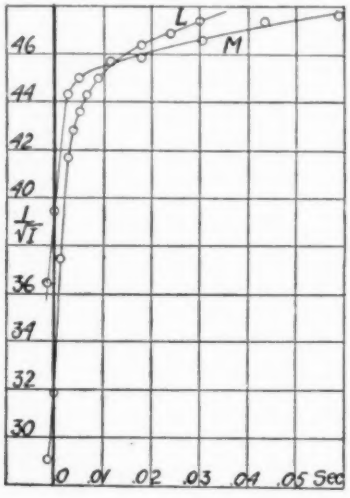

Fig. 4.

Showing effect of heat treatment.

Curve *L*. Willemite No. 1, time of excitation .022 sec.
" *M*. " " 2, " " " .022 "

curves were more difficult to obtain than those shown in Fig. 2 since the maximum wave-length, the one observed in every case, lies in the yellow-red, while the curves in Fig. 2 all have their maximum in the green. This difficulty, aside from the fact that the decay is less rapid, makes the points on these curves less certain than those of Fig. 2. It will be seen, nevertheless, that the curves have the same general shape and consist of the two straight lines merging into each other.

All of the substances mentioned are excited to fluorescence by

kathode rays to some extent, the $CdSO_4$ being especially brilliant, giving a very intense yellow. They were also found to be excited somewhat by X-rays, the $CdSO_4$ again showing the greatest intensity. In all cases the phosphorescence excited by X-rays was too small to be measured with the present apparatus.

The curves given in Fig. 4 show the change in the decay of willemite when heat-treated. Curve *L* shows the decay of the untreated willemite. Curve *M* shows the decay after heating the willemite for forty-five minutes at a bright red heat. It is clear from the

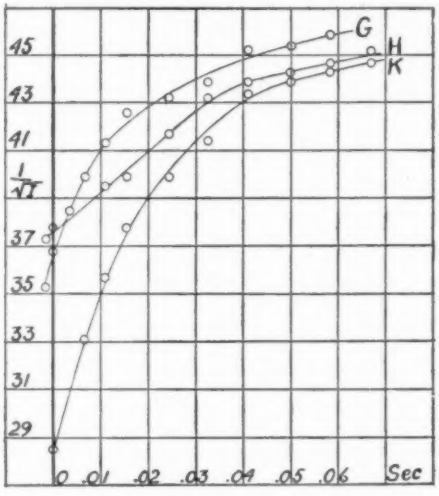

Fig. 5.

Curves showing effect of heat treatment.

Curve *H*. $ZnCl_2$ No. 1, time of excitation .031 sec.
" *K*. " " 2, " " " .031 "
" *G*. " " 3, " " " .031 "

curves that the heat treatment has decreased the initial intensity and made the decay less rapid ; both these changes may be observed by the eye alone if the two screens are excited in a dark room. Willemite no. 3 which had been heated two hours was found to give a curve whose points fell so nearly on curve *M* that it was not plotted.

The curves given in Fig. 5 show the decay in $ZnCl_2 + \times MnSO_4$ as affected by heat treatment. Curve *H* represents the decay in a sample of the substance taken as a dry powder, which resulted from the mixture in preparing and heating it only two hours at a bright

red. Curve *K* represents the decay of a sample heated five hours and curve *G* after seven hours heating. The curves show that the first heating was not sufficient to bring out the initial brightness and longer decay of the substance, and that there is a time limit to the heating necessary to produce maximum intensity; for on heating beyond this the initial intensity becomes less. From the behavior of this artificial compound it would seem that the natural willemite shown in Fig. 4 had reached a maximum heat treatment already, for further heating decreased its initial intensity. The slope of the curves in Fig. 5 seem to indicate little change in the rate of decay

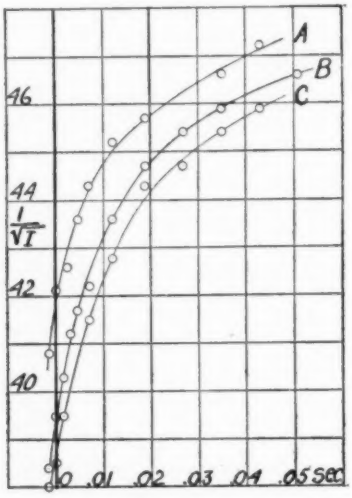

Fig. 6.

Showing the effect of changing the time of excitation.
Curve *A*. $ZnCl_2$ No 3, time of excitation .013 sec.
" *B*. " " " " " .024 "
" *C*. " " " " " .058 "

after the initial drop; unfortunately the intensity becomes so small that it was found impossible to carry the curves farther, and the readings in this region represent the average of a number of settings.

The curves given in Fig. 6. show the effect of decreasing the time of excitation in $ZnCl_2$ no. 3. This was accomplished by making the opening of the disc in Fig. 1 smaller. It was found that when 60-cycle current was used for the spark, the curves taken with decreased time of excitation were more or less irregular. This

was no doubt due to the fact that with the small opening of the disc the irregularities of the spark were more pronounced. However, on the 140-cycle current the curves were quite regular and could be duplicated very closely. The curves given in Fig. 6 were taken with the spark operated from the 140-cycle current and it will be noted that a decrease in the time of excitation brings about a more rapid decay.

The curves in Fig. 6 also serve to confirm, somewhat, the curves taken with the 60-cycle current; for it will be seen that they have the same general shape as those given for $ZnCl_2$ no. 3 in Fig. 2.

The Effect of Infra-Red on the Initial Decay of Sidot Blend.

The effect of infra-red on long-time phosphorescent substances has been studied,[1] and it was natural to suppose that short-time substances would be affected in somewhat the same way. The method of experimentation followed was to allow the light from the arc to fall on the phosphorescent screen through a piece of very

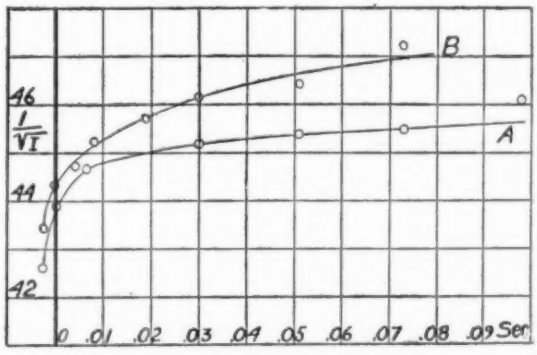

Fig. 7.

Curves showing the effect of infra-red on the initial decay of sidot blend.
Curve *A*. Without infra-red, time of excitation .04 sec.
" *B*. With " " " " " .04 "

dense ruby glass, and compare the shape of the decay curves taken with and without the infra-red. It was found, however, that none of the short-time substances were affected in measurable amount.

[1] Nichols and Merritt, PHYS. REV., Vol. XXV., p. 362, 1907.

There was a slight indication of some change in the shape of the latter portion of the decay curve, but the error in setting the spectrophotometer in this region where the light is so faint would account for the changes in the curves.

While the effect of infra-red on the decay of short-time phosphorescent compounds is so small that it cannot be readily measured, the effect of infra-red on sidot blend is quite marked.

In Fig. 7 curve *B*, showing the decay under the action of the infra-red, is the average of a number of determinations and the shape of the curve is fairly definite. However, this cannot be said of curve *A*, which is also the average of a number of trials, since the total intensity, over the range of time available, is very small. There is some doubt also as to the shape of the curve during the first hundredth of a second. It was necessary to change the position of the disc on the shaft of the phosphoroscope in studying the effect of infra-red and it is possible that the zero given may be incorrect, *i. e.*, the points on the zero ordinate and perhaps the one following may be in the fluorescent light, and therefore the real phosphorescent decay started at some later time than the zero given. This possible error in the zero only applies to the curves taken in studying the infra-red and in no way affects the other curves.

There is no question as to the effect of infra-red on the initial decay of sidot blend, but owing to the very slow decay, the shape of the curves may be more or less in error.

DECAY CURVES FOR DIFFERENT WAVE-LENGTHS.

The phosphorescence spectrum of each substance was studied and curves of decay taken for different wave-lengths to determine if all parts of the band, characteristic for each substance, decayed at the same rate. In all the substances studied the phosphorescence spectrum at room temperature consisted of a single band. The extent of each being as follows :

CaS_1	.53	to	.64	μ	with max. at	.575	μ.
$CdCl_2$	.545	"	.65	μ	"	"	" .59	μ.
$CdSO_4$	.514	"	.623	μ	"	"	" .565	μ.
$ZnCl_2$ no. 1	.49	"	.585	μ	"	"	" .52	μ.
Andrews $ZnCl_2$	.49	"	.545	μ	"	"	" .52	μ.
Willemite no. 1	.46	"	.56	μ	"	"	" .52	μ.

In order to determine the rate of decay of different parts of the band for any substance, two methods were used. One was to take a number of decay curves at different wave-lengths of the band and plot a curve showing the intensities at a fixed time after excitation, and the wave-lengths. The second method was to fix the axle of the phosphoroscope so as to reflect the light from the screen a certain time after excitation; then, by shifting the telescope of the spectrophotometer, to determine the intensity of the phosphorescence for the different wave-lengths; then adjust the phosphoroscope to give the decay at a later period, and in the same way measure the intensity for different wave-lengths. Both of these methods gave the same results, *i. e.*, that all portions of the band seemed to decay at the same rate. The curves shown in Fig. 8 are typical for all the substances studied.

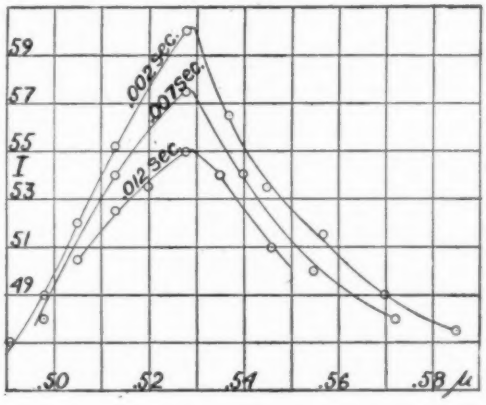

Fig. 8.

Curve showing the phosphorescent spectrum of $ZnCl_2$ no. 1, at different times after the exciting light was removed.

In none of the substances was there an indication of a shift of the maximum of the curve as the decay went on. If any change occurs during the decay it is too small to be detected by the method used.

Summary.

The most important points brought out by the experiments here described may be briefly stated as follows:

1. The decay curve when plotted with the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas consists of two straight lines gradually merging into each other. In this respect the short-time and long-time phosphorescent compounds seem to be similar.

2. The transition from fluorescence to phosphorescence is gradual, *i. e.*, the curve shows no sign of discontinuity.

3. The shape of the decay curve and the intensity depend upon the time of excitation.

4. The effect of heat treatment is such as to change both the intensity and the rate of decay of phosphorescence.

5. The effect of infra-red on short time decay substances, if it exists at all, is very slight; but its effect on the initial decay of sidot blend is quite marked.

6. The experiments indicate that all portions of the phosphorescence band present at ordinary temperatures decay at the same rate.

The writer wishes to express his gratitude to Professors Nichols and Merritt for encouragement and many valuable suggestions while this work was in progress.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

NEW BOOKS.

A Study of Splashes. By A. M. WORTHINGTON. 8vo, pp. xii + 129. London, Longmans, Green and Co., 1908.

Some of the results obtained by Mr. Worthington in his extremely interesting photographic study of splashes are already more or less familiar, since papers dealing with the subject have appeared in the Philosophical Transactions. The book before us deals with the subject in a less technical way and is intended for the general reader as well as for the physicist. The numerous photographs of splashes — 197 in all — are chosen for their beauty as well as for their appropriateness in illustrating different phases of the phenomena, and are well reproduced. The apparatus used in obtaining the photographs is described, and the fundamental principles involved in the formation of splashes are also briefly but clearly explained.

The photographs reproduced and discussed form seventeen series, each dealing with the splash occurring under one definite set of conditions. Series I., for example, consists of thirty photographs of the splash formed when a drop of water falls into a mixture of water and milk. The successive stages of the splash are shown, from the instant the drop strikes the surface until the disturbance has almost subsided. The photographs are remarkably clear and enable the phenomena to be studied in the greatest detail. The photographs of Series I*a*, showing the splash of water falling into water, are even more interesting and beautiful. Other series show the results obtained with different heights of fall, by using smooth or rough spheres of various sizes and materials instead of drops, and by varying the liquid used. In many cases a special arrangement of apparatus was employed which allowed the falling sphere to be followed after it had passed below the surface. Several photographs are also shown of the "splashes" produced in armor plate by the impact of a projectile.

E. M.

Vorlesungen über Technische Mechanik. By A. FÖPPL. Vol. V. 8vo, pp. xii + 391. Leipzig, Teubner, 1907.

The fifth volume of Föppl's lectures on Technical Mechanics deals with "the most important problems of the higher theory of elasticity." The book is not intended as a text-book, even for the German technical schools, where so much more is expected of the student along the lines

of mathematics and pure science than is demanded in this country. The author does not expect the student to read carefully and consecutively, but rather to obtain by rapid reading a general idea of the topics treated, so as to be able to make use of the book later when special problems arise. In other words the book is intended as a reference book for those engaged in such problems of design as require something more than the usual elementary procedure.

The following titles of the chapters will indicate the scope of the work: I., Condition of Strain and Danger of Rupture; II., Theory of Elasticity in the Case of Plates; III., Torsional Elasticity of Prismatic Rods and Bodies of Revolution; IV., Bodies of Revolution with Axially Symmetrical Loading; Strains Due to Heat; V., General Laws for the Work Involved in Change of Form; VI., Various Applications.

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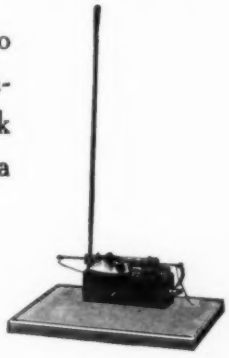

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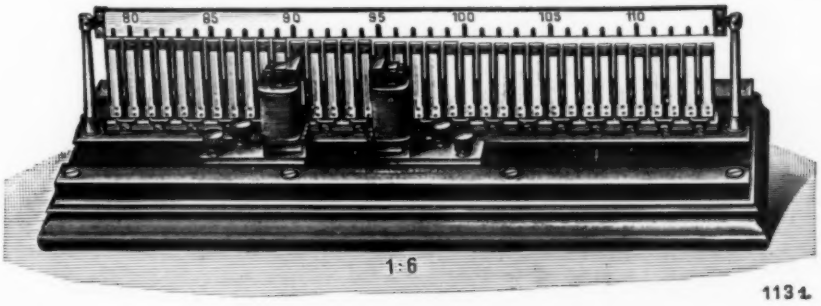

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